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Catalytic Upgrading of Biomass Model Compounds: Novel Approaches and Lessons Learnt from Traditional Hydrodeoxygenation – a Review

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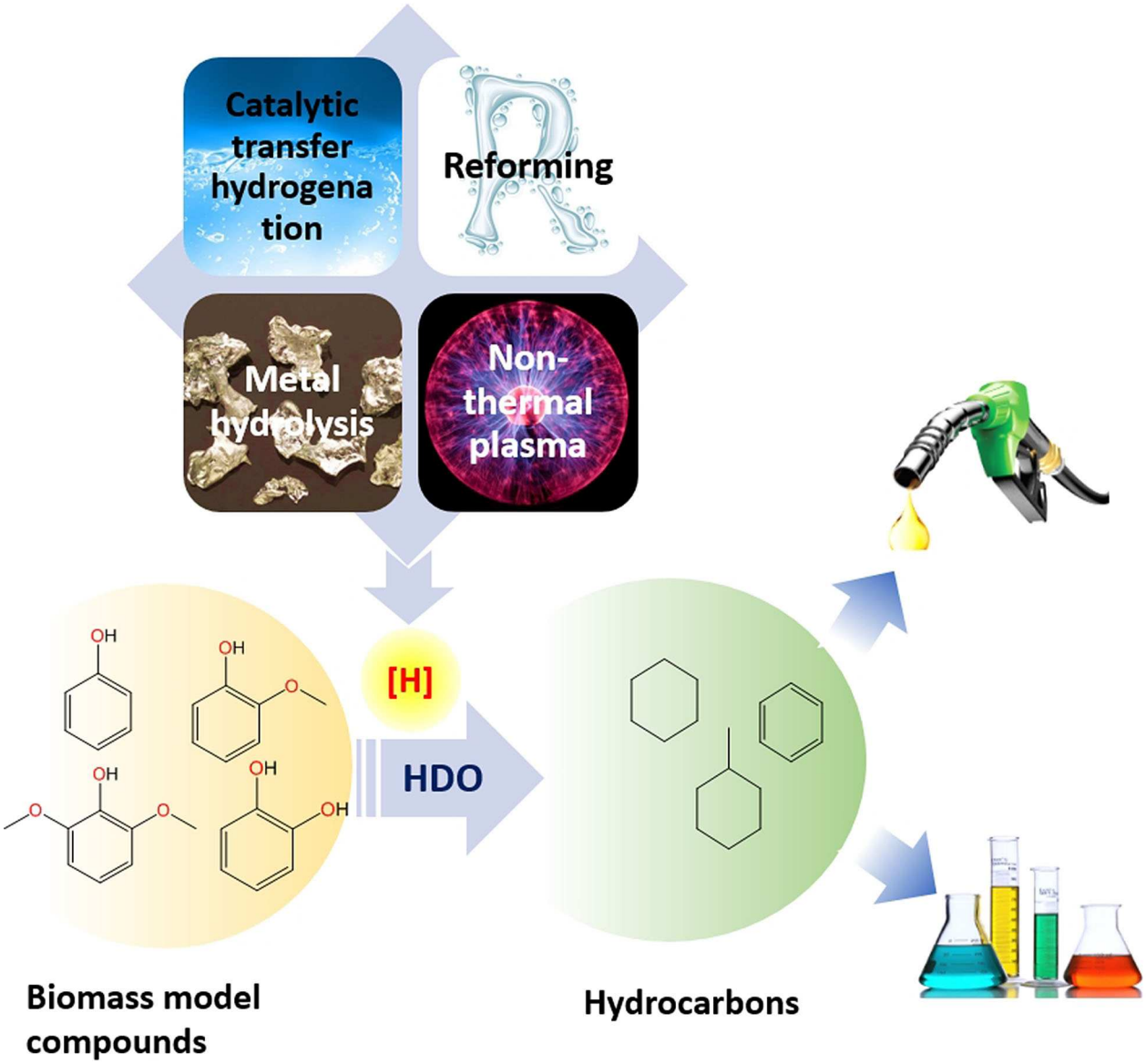

Catalytic hydrodeoxygenation (HDO) is a fundamental process for bio-resources upgrading to produce transportation fuels or added value chemicals. The bottleneck of this technology to be implemented at commercial scale is its dependence on high pressure hydrogen, an expensive resource which utilization also poses safety concerns. In this scenario, the development of hydrogen-free alternatives to facilitate oxygen removal in biomass derived compounds is a major challenge for catalysis science but at the same time it could revolutionize biomass processing technologies. In this review we have analysed several novel approaches, including catalytic transfer hydrogenation (CTH), combined reforming and hydrodeoxygenation, metal hydrolysis and subsequent hydrodeoxygenation along with non-thermal plasma (NTP) to avoid the supply of external H_2. The knowledge accumulated from traditional HDO sets the grounds for catalysts and processes development among the hydrogen alternatives. In this sense, mechanistic aspects for HDO and the proposed alternatives are carefully analysed in this work. Biomass model compounds are selected aiming to provide an in-depth description of the different processes and stablish solid correlations catalysts composition-catalytic performance which can be further extrapolated to more complex biomass feedstocks. Moreover, the current challenges and research trends of novel hydrodeoxygenation strategies are also presented aiming to spark inspiration among the broad community of scientists working towards a low carbon society where bio-resources will play a major role.

1. Introduction

The development of renewable energy, including biomass, solar, hydropower, wind, geothermal energy, *etc.* has become an inevitable step in view of the growing demand of energy and the dramatic climate change. Biomass plays an irreplaceable role in renewable energy portfolio, occupying 75% of the total renewable energy consumption.[1] It has unique advantages over other renewable energy in producing fuels and high-value chemicals with very limited carbon footprints.[2] Therefore, biomass exhibits great application potentiality in the transition towards a new energy paradigm. For example, "The Energy Strategy 2020" projection[3] proposed by European Commission, recommended the use of biomass, which is expected to occupy 56% of the total renewable energy in EU27 countries by 2020. The International Renewable Energy Agency (IRENA) launched a programme, called "Remap 2030",[1] conjectured the increasing developing tendency of biomass energy. It is speculated that solid and liquid biomass usage amount will increase by four and six times respectively, between 2010 and 2030 indicating a promising future for this green resource.

Biomass is the sole renewable organic carbon source in nature which possesses plenty of excellent advantages such as abundance, low price, diversity and wide distribution.[4] Lignin, along with hemicellulose and cellulose, are the three main components of biomass. Lignin accounts for 10%–35% by weight and up to 40% by energy in biomass feedstocks[5] and 20%–35% of the dry mass in woody biomass.[6] However, its complex structure and high thermal stability limits the commercial utilization of lignin. Presently, the main application of lignin is being burned as low-value fuel, which is apparently not a sensible choice from the perspective of economy and sustainability.[7] Nevertheless, lignin possesses a great potential for producing high-value chemicals (especially aromatics) and transportation fuels since it is a complex three-dimensional amorphous polymer composed of a number of phenylpropane-units (C9 units) linked through a plenty variety of C–O and C–C bonds.[8] The three basic phenylpropane monomers presenting in the lignin structure are: (1) *p*-coumaryl alcohol; (2) coniferyl alcohol; (3) sinapyl alcohol (Figure 1).[9] The concentration of these phenylpropane-units varies with the species of feedstocks and separation method. The exact structure of lignin is still established subject of debate.[10]

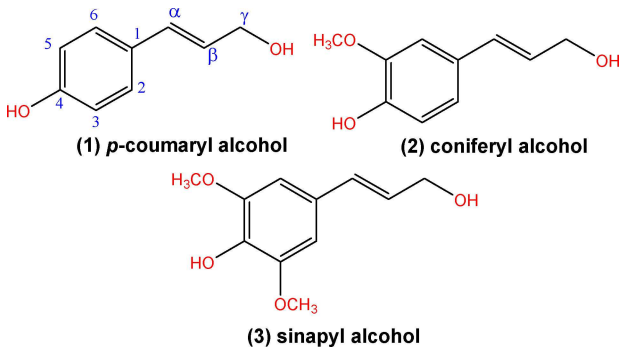

Figure 1. Three basic phenylpropane monomers: (1) *p*-coumaryl alcohol; (2) coniferyl alcohol; (3) sinapyl alcohol.

Pyrolysis is one of the thermo-chemical conversion technologies for producing bio-oil directly from biomass feedstocks.[11] Pyrolysis is an effective technique for the utilization of lignin since it could convert lignin waste (*i.e.* black liquor) into high-value fuel and chemicals, achieving both economic and environmental benefits.[12] Notable differences in the product

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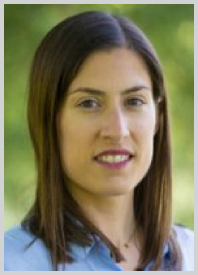
Sai Gu joined the University of Surrey as Head of the Department of Chemical and Process Engineering in 2015 after holding various academic posts at Aston University, the University of Southampton and Cranfield University. He obtained a Ph.D degree in material modelling from the University of Nottingham and also performed post-doctoral research at the University of Cambridge. Prof. Gu owns an international reputation for clean energy and material research. He is currently leading a number of EPSRC-funded projects focused on the development of advanced bio-energy technologies.



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distribution from pyrolysis process can be observed considering the diverse origins and extraction method of lignin.[13] Generally, higher methoxyl content exists in lignin from hardwood (*e.g.* leaved trees) than that of lignin from softwood (*e.g.* resinous trees) considering the higher content of syringyl units in the former.[13b] Several methods, such as hydrochloric acid, Klason, enzymatic and steam explosion are employed to carry out the separation of lignin from lignocellulose feedstocks.[14] However, it is impossible obtain identical lignin sample from heterogeneous biomass since the structure changes during the separation procedure, even using the same separation method.[15] In general, lignin- derived pyrolytic oils contain large amount of oxygenated chemicals (oxygen concentration: 35–40 wt.%).[16] The dominating fraction, phenolics, yield 25–40 wt.% (with 7–11 wt.% monomers) derived from fast pyrolysis of lignin.[17] Typically, lignin-derived monomeric phenolics mainly include phenol, guaiacol, anisole, *p*-cresol, *m*-cresol and vanillin (Figure 2), which are widely employed as model compounds of

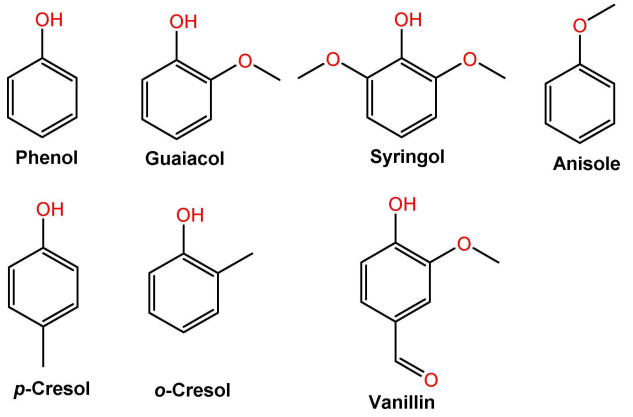

Figure 2. Molecular structures of typical monophenolic model compounds of lignin.

lignin to reduce the complexity in reactivity and mechanism studies. The presence of oxygen-containing compounds results in deteriorated properties, such as serious corrosivity (high acidity), low heating value, thermal and chemical instability, immiscibility with conventional fuels, *etc.*[18] making lignin-derived bio-oils not suitable for their direct utilization as liquid fuel in the petrochemical industry.[19] Hence, lignin-derived bio-oil upgrading is an essential procedure required to convert bio-oil into a deoxygenated fuel with comparable physicochemical features than those exhibited by petroleum oils. Giving the complexity of the bio-oil molecules, the use of model compounds is advisable to discern mechanistic information which is indispensable to guide the catalysts and process design.

Therefore, in this work we review the catalytic hydrodeoxygenation (HDO) process of lignin-derived monophenolics (model compounds) given their key guidance role in bio-oil upgrading technologies.

Deoxygenation process can upgrade bio-oil by selective removing the oxygen-containing groups from the reactant to produce saturated hydrocarbons or aromatic hydrocarbons.[20] Hydrodeoxygenation (HDO) is a prominent process for oxygen removal from oxygen-containing compounds through catalytic process to produce high energy hydrocarbons with low emission. HDO exhibits remarkable advantages as low reaction temperature, high efficiency of eliminating of oxygen atoms and preserving the carbon number in the products.[21] This process requires a hydrogen source, which could be external H_2, hydrogen donor solvent or even the reagent itself. HDO process typically occurs via hydrogenolysis of C–O bonds over heterogeneous catalysts with subsequent elimination of oxygen in the form of water. Different types of reactions are likely to happen during HDO process, including decarboxylation, hydrogenation, hydrogenolysis, hydrocracking and dehydration (Figure 3). Considering the complex composition of lignin-derived bio-oil and the difficulty of the deconvolution of resultant possible reaction pathways during deoxygenation process, most HDO investigations employ the dominating monophenolic oxygenates to obtain fundamental mechanistic understanding of bio-oil upgrading process and establish optimal condition in converting the phenolic-rich bio-oil into transportation fuel.[22] Regarding to deoxygenated products produced from HDO process of phenolic compounds, aromatic hydrocarbons and cyclohexanes are always envisaged as target products separately. These two types of products have different chemical implications. Aro-

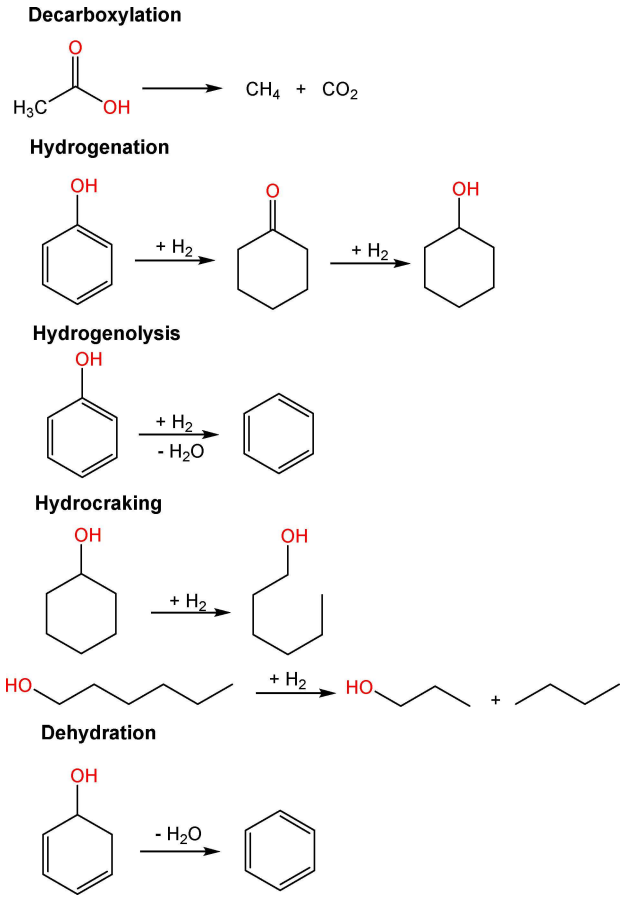

Figure 3. Possible reactions in HDO process (adopted from ref. [22]).

matic hydrocarbons, such as benzene and toluene are high-value chemicals in chemical industry while cyclohexanes, such as cyclohexane, are important chemical intermediates which can be used as oxygen-free transportation fuel. It is generally accepted that HDO of phenolic lignin model compounds processed through three distinct routes (Figure 4): (1) direct

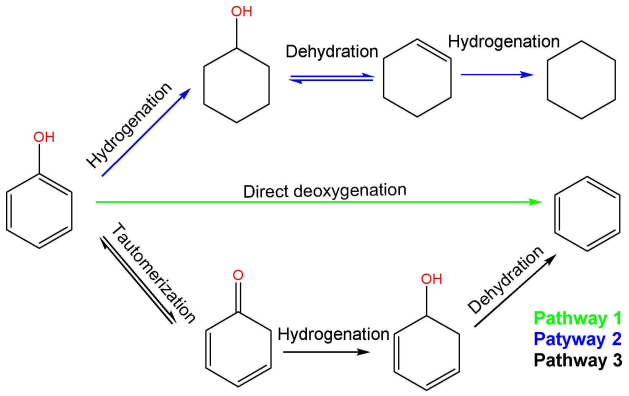

Figure 4. Possible reaction pathways in HDO process of phenol: (1) DDO; (2) HYD; (3) tautomerization-deoxygenation (adopted from ref. [24]).

deoxygenation route yielding aromatic compounds (DDO pathway);[23] (2) hydrogenation-dehydration route yielding cycloalkenes and cycloalkanes (HYD pathway); (3) tautomerization-deoxygenation route yielding aromatic compounds.[24] The first two routes are more common in HDO process. The C–O bond is directly cleaved from the oxygen-containing chemicals via hydrogenolysis without the intermediate hydrogenation steps for DDO pathway. Typically, high temperature and low hydrogen pressure is beneficial for the DDO pathway whereas HYD route is favoured in the opposite situation *i.e.* low temperature and high hydrogen pressure.[25] DDO pathway is more profitable than the HYD pathway since it does not require the hydrogenation of benzene rings for oxygen removing. Accordingly, DDO pathway will require less external H_2 supply and will produce aromatics with higher octane ratings which are more suitable for the purpose of oil blending.[26] The type of reaction routes happening during the phenolics HDO process will be dependent on catalysts' formulation and reaction conditions such as temperature and hydrogen pressure.[27]

Recently, novel strategies are being developed for upgrading lignin-derived bio-oil and model compounds in which other hydrogen sources were used to replace molecular hydrogen, considering the high cost of H_2 production and potential risk in terms of transportation and storage. These strategies can be summarized into four categories according to the reaction mechanisms: (1) Catalytic transfer hydrogenation (CTH) process which can be realized through direct hydrogen transfer and/or metal hydride route;[28] (2) Reactions involving two consecutive steps: H_2 production from aqueous-phase or gaseous-phase reforming reaction, followed by HDO process;[29] (3) Metal-hydrolysis for production hydrogen with subsequent *in-situ* HDO;[30] (4) Non-thermal plasma (NTP) oxygen-removal method.

Numerous reaction parameters can affect the efficiency of HDO process, including type of reactor, catalyst selection, temperature, hydrogen pressure, solvent, time on steam (TOS), weight hourly space velocities (WHSV), *etc.* Among all of them, the catalyst always plays a central role and it can be regarded as the philosopher's stones in HDO process. The catalysts design constitutes the main focus of researchers given its imperative role in the reaction mechanism and overall efficiency of the HDO process. In contrast, solvent's effect deserves more attention for obtaining a comprehensive understanding of HDO process. Herein, in this review, the discussion on the performance of both catalyst and solvent in the metal-catalysed HDO of lignin-derived monomeric phenolic compounds using H_2 was presented in an attempt to serve as a helpful guide towards the development of efficient catalysts in HDO process. In addition, alternative methods for oxygen removal of lignin-derived phenolic compounds without external H_2 supply will be discussed in this review for the first time. The bottlenecks and perspectives of lignin-derived bio-oil HDO process will be also presented to provoke further breakthrough of bio-oil upgrading without using high cost external molecular hydrogen. These insights will be useful for the catalyst selection and the optimization of reaction conditions which are key aspects to consolidate biomass processing technologies as competitive routes for clean energy production.

2. Hydrodeoxygenation Using H_2

Presently, hydrodeoxygenation (HDO) process with external H_2 supply is the most common method used for bio-oil upgrading. HDO is typically carried out at relatively low reaction temperature (200-400 °C) and high hydrogen pressure in a batch-wise autoclave reactor (4-20 MPa) or a continuous-flow fixed-bed reactor (5–10 MPa).[31] It happens by removing oxygen in the form of water with the participation of H_2 [Eq. (1)].

Hydrodeoxygenation (HDO):

$$R{-}OH + H_2 \rightarrow R{-}H + H_2O \quad (1)$$

Catalyst and solvent play crucial roles for the conversion of reactant and the distribution of HDO products. Herein, a discussion in terms of catalyst's and solvent's effect on HDO of lignin-derived monophenolic compounds are presented. Our critical summary aims to provide key indications for developing efficient catalyst, selecting solvent and optimizing reaction parameters in bio-oil upgrading process.

2.1. Catalyst's Effect

Traditionally, transition metal catalysts have been used in catalytic hydrogenation of bio-oil or lignin-derived model compounds in view of the high H_2 sticking probability and the ability of transition metals to activate hydrogen.[18a] The design of HDO catalyst was inspired by the formulation of hydrodesulfurization (HDS) catalysts used in the petroleum upgrading

process for removing sulfur contaminants.[32] Conventional HDO catalysts are Al_2O_3 supported sulfided CoMo or NiMo catalysts.[33] In these catalysts, MoS_2 acts as the active sites and Co or Ni as the promoter. It is well accepted that Ni or Co could donate electrons to Mo and lead to a weakening of the metal-sulfur bond,[34] which related to the amount of labile sulfur in the active phase.[35] Besides, the addition of promoter could enhance the mobility of sulfur, resulting in the creation of more surface vacancies which perform as the active sites for both HDS and HDO processes.[36] Although these catalysts have excellent HDO capacity, problems can still be observed in bio-oil upgrading process. On the one hand, the maintenance of catalysts' activity needs the introduction of sulphur-containing compounds (*e.g.* H_2S), which could result in problems like sulphur contamination and H_2S emissions.[37] One the other hand, Al_2O_3 shown to be an inappropriate support due to the fact that the water formed in HDO process and oxygen-containing substances could convert it into boehmite (AlO(OH)).[38] It is accepted that the high affinity for carbon formation on the surface Al_2O_3 and the high acidity of Al_2O_3 (Lewis acid sites) could result in the deactivation of catalyst.[39] Therefore, it is important to develop stable catalysts with the aim to obtain uncontaminated value-added chemicals or transportation fuels.

Similarly, to most of the heterogeneously catalysed reactions, both the support and the active phase have constituted the main research concern in the design of effective HDO catalysts. Support should not be overlooked since it plays an important role of stabilizing the active catalytic particles in a highly dispersed form. Also, some supports can be active in the reaction and help to overcome reactants activation and facilitate the active phase-reactant encounter due to an enhanced metal-support interaction. In this scenario, electronic, acid-base and textural properties of the support are of paramount importance and heavily impact the overall catalysts design. Conventional supports for HDO catalyst are acidic γ-Al_2O_3. Typically, this standard support has to be embedded in multifunctional materials (*i.e.* a bifunctional catalyst). A bifunctional catalyst is defined as a catalyst which is able to display two functions. Importantly, both functions can be displayed by just the metal (active phase) or one function by the metal and the other by the support. Typically, bifunctional catalysts contain both metal (such as commercial heterogeneous catalysts or metal particles) and acid components which including liquid acid (acidic ionic liquids,[40] mineral acid,[41] *etc.*) or solid acid (γ-Al_2O_3,[42] zeolite,[43] Nafion/SiO_2,[44] *etc.*). The application of bifunctional catalysts in phenolics HDO process is not uncommon, especially for catalysts in which metals have low deoxygenation activity (*i.e.* Pt, Ru, Pd). Two different active materials (metal and acid compounds) can provide catalytic sites needed to perform the different types of elementary reaction steps in HDO process.[45] In general, the hydrogenation of C=C and C=O bonds are mainly favoured by noble metal component, while hydrocracking, dehydration and isomerization are mainly promoted by acid sites, resulting the complete deoxygenation of phenolics[46] in bifunctional catalytic systems. Consequently, bifunctional catalysts require lower hydrogen pressure than those required for direct C–O bond cleavage over metal nanoparticles alone.[47] It should be noted that Lewis acid site density and Brønsted acid density perform different roles in HDO process, in which the former binds species to catalytic surface while the later protonates the intermediates.[48] Recently, bifunctional catalysts have drawn great attention in HDO process for upgrading bio-oil as reflected in several reviews articles where a comprehensive evaluation of their influence was discussed.[45,49] However, compared with neutral supports, acidic supports showed a lower stability in the HDO of phenolic compounds.[46e,50] Despite the fact the acidic materials help to overcome some of the reaction steps they are prone to coke and typically suffer for rapid deactivation. In this sense, besides conventional Al oxides catalysts, it is worth to mention that oxophilic supports, such as ZrO_2 and TiO_2, typically showed higher selectivity of aromatic compounds and less susceptibility for carbon deposition[24,51] in phenolics HDO process. A keto-intermediate tautomer favoured by the oxophilic sites could explain the efficient performance of these oxophilic support-containing catalysts.[51]

The effect of the active site (metallic element) has a great influence on the product distribution of phenolics HDO process. Conventionally, transition metal based catalysts could be classified into two categories: non-noble and noble metal based catalysts. The latter involves economic considerations, metal availability and reactivity factors. The choice of the metallic phase has a strong impact on the conversion, selectivity and stability of catalyst, therefore, in the following section, the role of different transition metal-based catalyst in phenolics HDO process is discussed in detail.

2.1.1 Monometallic Catalysts

2.1.1.1 Non-Noble Transition Metals

Non-noble transition metal-based catalysts (for example those using Ni, Co, Fe, Mo, *etc.* as active phase) are commonly studied in HDO process for the upgrading of bio-oil or lignin-derived phenolic compounds. Typically, non-noble transition metallic catalysts such as Co, Fe, Mo, favour the DDO pathway to produce aromatic hydrocarbons in HDO process of phenolics. In contrast, Ni-based catalyst typically supported on acidic support can effectively convert phenolic compounds into cyclohexanes.

Ni-Based Catalysts

Nickel (Ni) and nickel phosphide (Ni_2P) supported catalysts have been used as the monometallic catalysts for HDO of phenolic lignin model compounds. Ni-based catalysts are highly active for the hydrogenation of aromatic rings due to the high hydrogenation activity of Ni.[52] Ni metal has a relatively lower electrophilicity compared to other non-noble transition metals such as molybdenum (Mo), making it less prone to overcome the activation and direct scission of C=O and C–O bonds.[53] Hence, the deoxygenated products obtained during HDO

reactions catalysed by monometallic Ni catalyst are mainly cyclohexanes instead of aromatic hydrocarbons. Different parameters could affect reaction pathways and distribution of products. Hydrogenation and deoxygenation reactions of phenol over Ni/SiO_2 catalyst were found greatly depending on Ni-particle size. A kinetic study showed that a Ni particle size (*d*) of 9–10 nm seems optimal for deoxygenation at temperature below 300 °C.[54] The type of support can also affect reaction pathways in HDO of phenol over Ni-based catalysts. It was speculated that over SiO_2 supported Ni catalyst, the phenol was firstly hydrogenated to cyclohexanol followed by dehydroxylation to form cyclohexane (Figure 5, route 2). In contrast, Lewis

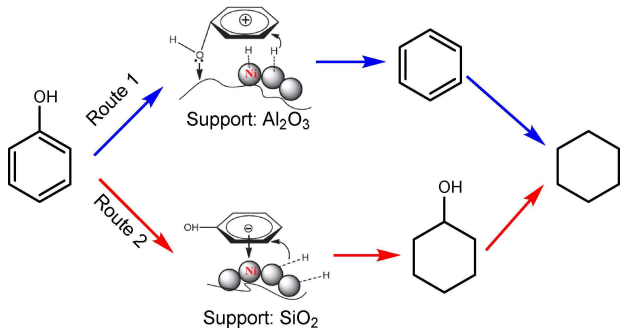

Figure 5. Possible reaction pathways for the phenol HDO reaction over γ-Al_2O_3 or SiO_2 supported Ni-based catalysts (adopted from ref. [55]).

acid sites in the surface of Ni/γ-Al_2O_3 could activate C–O bond, resulting in the heterolytically cleave to form intermediate benzene followed by the production of cyclohexane via hydrogenation reaction (Figure 5, route 1).[55] The use of combined support SiO_2-Al_2O_3 in Ni-based catalytic system exhibited high activity in syringol HDO process, in which 100% conversion with 97.8% selectivity for cyclohexane was obtained at 200 °C, 2 MPa H_2 pressure, superior than the performance of individual Ni/SiO_2 or Ni/Al_2O_3 catalyst.[56] The simulating existence of high Ni dispersion and high amount of acid sites contributed to the excellent HDO performance of SiO_2–Al_2O_3 supported catalyst. The proposed main reaction pathways over Ni /SiO_2–Al_2O_3 was presented in Figure 6. Typically, demethoxylation and dehy-

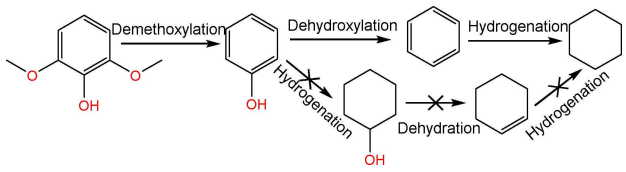

Figure 6. Proposed main reaction pathways for syringol HDO over Ni/SiO_2-Al_2O_3 catalyst (adopted from ref. [57]).

droxylation happened to produce benzene in the early stage. Subsequently, cyclohexane was formed through the hydrogenation of benzene. In contrast, the hydrogenation-dehydration-hydrogenation pathway was not observed. Comparing with the reaction pathway of Ni/γ-Al_2O_3 and Ni/SiO_2 (Figure 5),[55] it can be summarized that the influence of γ-Al_2O_3 on reaction pathway is more dominant than that of SiO_2 in the Ni/SiO_2–Al_2O_3 catalytic system.

Carbon is another promising support used in HDO process in combination with Ni nanoparticles. In general terms carbon is commonly used in catalytic applications due to its excellent textural and mechanical properties, its ability to anchor metal particles leading to high metallic dispersion[57] and its lower price compared with traditional alumina and silica supports. Moreover, the amphoteric characteristic of carbon-based materials facilitates metal nanoparticles deposition and the metal-support interaction. Recently, carbon-based solids and in particular, carbon nanotubes (CNTs) have been developed and widely used as supports in HDO catalysts. CNTs have drawn great attention due to their unique characteristic like electrical properties, hydrogen spillover capacity, chemical stability in aggressive media and inert surface,[58] which show great potential for the utilization in HDO process as carriers. Dongil *et al.*[59] investigated the different catalytic behaviour of Ni nanoparticles loaded inside and outside of commercial CNTs in guaiacol HDO process. Results showed that Ni located inside the CNTs favoured the formation of cyclohexene while the opposite location favoured the formation of cyclohexane. It is speculated that the distinction in selectivity can be ascribed to the effect of steric constraints, which dictate the adsorption mode of cyclohexene in the Ni/CNT catalyst.[59] In addition, doping carbon with different promoters could enhance its electronic properties and positively affect the catalytic process. For instance, nitrogen-doped carbon black (NCB) materials are recognized as superior candidates to be used as catalyst supports due to their excellent electrical conductivity and rich pore structure.[60] Indeed, Nie and co-workers successfully applied a series of catalysts based on Ni nanoparticles supported on porous NCB-900 showing remarkable performance at mild condition (T = 150 °C P = 0.5 MPa) on the partial HDO of vanillin to produce 2-methoxy-4-methylphenol (conversion ≈ 100%, selectivity ≈ 100%). Overall, this result outperforms that reached by frequently-used Ni-based catalysts (*i.e.* Ni/carbon black, Ni/active carbon, Ni/SiO_2 and Ni/MgO). The high catalytic activity could be attributed to the specific characteristics of Ni/NCB and the intimate interaction between the Ni and the N species.[61]

Ni_2P-based catalysts have been extensively studied for HDO process of various phenolic compounds.[62] Ni_2P exhibits superior HDO performance to Co_2P, Fe_2P, WP and MoP, which is ascribed to the higher *d*-electron density of Ni_2P phase and a combination of structural and electronic influences of P atoms on the Ni metal sites, resulting in an easier oxygenate adsorption and breakage of C–O bond.[63] Ni_2P also exhibited a better stability than commercial sulfided $CoMo/Al_2O_3$ catalysts.[63a] It was reported that high reaction temperature and low H_2 pressure (*e.g.* 400 °C and 0.5 MPa) was favourable for the production of benzene, while low reaction temperature and high H_2 pressure (*e.g.* 300 °C and 1.5 MPa) aid the formation of cyclohexane over Ni_2P/SiO_2 catalyst for phenolic mixtures (anisole: phenol = 1:1 (*w/w*)) and guaiacol HDO process.[25c] The

size of Ni_2P can also affect partial positive charges of Ni cation and further influence the distribution of deoxygenation products. An opposite tendency was observed between the strength of Ni–P interaction and particle dimeter of Ni_2P cluster in Ni_2P-based catalysts (Ni_2P/SBA-15 and Ni_2P/SiO_2). Small Ni_2P clusters have stronger Ni–P interaction than large ones on silica. The collaboration of small Ni_2P clusters and Brønsted acids promoted a combinative dehydration-hydrogenation route for converting the intermediate, 4-methylcyclohexanol, into methylcyclohexane in 4-methylguaiacol HDO process.[64] A comparison of the product evolution route over Ni_2P/SiO_2 and Ni_2P/*h*-ZSM-5 (hierarchical ZSM-5) catalysts indicated that the bifunctional Ni_2P/*h*-ZSM-5 catalyst was effective for the production of total deoxygenated product, methylcyclohexane (selectivity ≈100%), in *m*-cresol HDO process, significantly superior to Ni_2P/SiO_2 catalyst due to the coexistent of metal active sites and Brønsted acidity from the zeolite support. Besides, bifunctional Ni_2P/*h*-ZSM-5 catalyst leaded to new reaction pathways compared with Ni_2P monometallic catalyst for HDO of *m*-cresol. Initially, Ni_2P/SiO_2 produced 3-methylcyclohexanol followed by the secondary reaction to produce methylcyclohexane. In contrast, Ni_2P/*h*-ZSM-5 catalysts exhibited far more rapid conversion of intermediate methylcyclohexanol, before producing the final deoxygenated product, methylcyclohexane (Figure 7).[65]

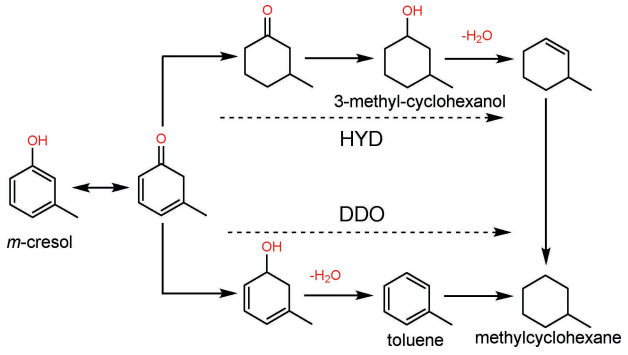

Figure 7. Proposed reaction pathways in *m*-cresol HDO process over Ni_2P/*h*-ZSM-5 (adopted from ref. [65])

In general, Ni-based catalysts are promising for HDO process. However, the improvement of Ni-based catalysts is still on-going. Ni metal shows a lower electrophilicity compared with other transition metals like molybdenum (Mo). Reactions like hydrogenation, decarbonylation and decarboxylation were often observed while the direct scission of C=O and C–O bonds is not the predominant reaction.[66] In addition, Ni metals can be oxidized easily in air and the catalytic activity decrease gradually with the storage time. Nevertheless, the deoxygenation activity could be improved by synergizing with other electrophilic metals or using suitable supports with deoxygenation ability.

Co-Based Catalysts

Cobalt (Co) is also one of the transition metals which has been widely studied for HDO of phenolic compounds. Co-based catalysts exhibit higher catalytic performances compared with other transition metal, such as Ni, in terms of the production of aromatic hydrocarbons due to the high efficiency in the removal of oxygen by DDO route.[26,67] The possible HDO mechanism of guaiacol over Co/SiO_2 catalyst is showed in Figure 8.[26] The HDO process proceeds through H_2 activation on

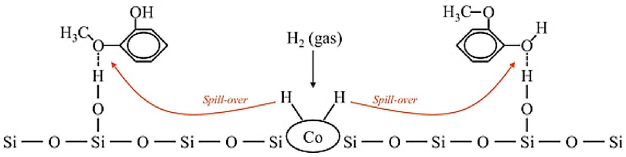

Figure 8. Possible mechanism of guaiacol conversion into aromatic hydrocarbons by HDO over Co/SiO_2 catalyst (reprinted from ref [26] with permission of Elsevier. Copyright 2014 Elsevier).

Co and the subsequent hydrogen spillover towards guaiacol in which hydrogenolysis of C_{Ar}-O-CH_3 bond seems to be preferential over that of C_{Ar}–O–H bond.[68]

Besides, cobalt nitride (CoN_x) and cobalt phosphide (Co_xP_y) catalysts have demonstrated excellent performance in HDO process. For example, CoN_x supported on N-doped carbon (NC) was effective for selective cleavage of C_{aryl}-OR bond in HDO process of lignin model compound, eugenol. In contrast, the Co/NC showed weak deoxygenation ability at the same reaction condition, with >99% of non-deoxygenated products. Results indicated that the interaction between Co and N resulted in the deoxygenation ability of CoN_x/NC catalyst.[69] In addition, it has been reported that the Brønsted acidic sites were attributed to the P-OH species in Co_xP_y/SiO_2 catalytic system.[70] The activity of Co_xP_y/SiO_2 catalysts were related to the stoichiometry of the active phase formed (Co_xP_y). Catalysts comprising CoP as the main active phase showed the most excellent catalytic behaviour in phenol HDO process.[71]

It has to be mentioned at this point that Co is mainly used as promoter for different catalytic systems given its ability to boost the DDO/HYD ratio in HDO of phenolic compounds,[72] rather than used as monometallic catalyst itself. In other words, when compared to Ni, Co is not normally envisaged as an active phase on its own while Ni is a standard choice for monometallic noble metal free catalysts in HDO reactions. Table 1 reports some examples of Ni and Co based catalysts employed in HDO processes of lignin model compounds and evidences the superiority of Ni over Co as main active phase in terms of the HDO activity.

Fe-Based Catalysts

Iron (Fe) is another promising candidate as catalyst for bio-oil upgrading through HDO process,[73] which shows advantages

Table 1. Transition metal (Ni, Co)-based catalysts for HDO of phenolic compounds.

Catalysts Metal	Support	Solvent	Reaction conditions T [°C]	P [MPa]	Model compounds t [h]	Major products	Sel. [%]	Conv. [%]	Reactor	Ref.
Ni	γ-Al_2O_3	*n*-octane	300	5	16	phenol	cyclohexane	≈88	≈100	batch [55]
Ni	SiO_2	*n*-octane	300	5	16	phenol	cyclohexane	≈90	≈99	batch [55]
Ni	SiO_2-Al_2O_3	decalin	200	2	2	syringol	cyclohexane	97.8	100	batch [56]
Ni (d = 5 nm)	SiO_2	–	275	10	5	phenol	cyclohexane	≈78	41	batch [54]
Ni (d = 22 nm)	SiO_2	–	275	10	5	phenol	cyclohexanol	≈92	100	batch [54]
							cyclohexane	≈5		
Ni	CNT (outside)	–	300	5	2	guaiacol	cyclohexanol	≈55	100	batch [59]
							cyclohexane	≈22		
							cyclohexene	<5		
Ni	CNT (inside)	–	300	5	2	guaiacol	cyclohexanol	≈64	100	batch [59]
							cyclohexane	≈15		
							cyclohexene	≈8		
Ni	NCB-900	water	150	0.5	5	vanillin	2-methoxy-4-methylphenol (MMP)	≈100	≈100	batch [61]
Ni_2P	SiO_2	–	300	1.5	5	anisole: phenol = 1 : 1 (*w/w*)	cyclohexane	96.7	100	fixed-bed [25c]
							benzene	3.3		
Ni_2P	SiO_2	–	400	0.5	5	anisole: phenol = 1 : 1 (*w/w*)	cyclohexane	4.3	100	fixed-bed [25c]
							benzene	95.7		
Ni_2P	SiO_2	–	300	1.5	5	guaiacol	cyclohexane	96.5	91.0	fixed-bed [25c]
							benzene	3.5		
Ni_2P	SiO_2	–	400	0.5	5	guaiacol	cyclohexane	5.0	91.7	fixed-bed [25c]
							benzene	74.0		
							phenol	21.0		
Ni_2P	SiO_2 (Low surface area)	*n*-hexadecane	250	4	8	4-methyl guaiacol	cresol	20.3	88.4	batch [64]
							4-methylcyclohexanol	37.4		
							methylcyclohexane	32.7		
Ni_2P	SiO_2 (High surface area)	*n*-hexadecane	250	4	8	4-methyl guaiacol	cresol	18.0	87.2	batch [64]
							4-methylcyclohexanol	35.5		
							methylcyclohexane	37.9		
Ni_2P	SBA-15 (meso-)	*n*-hexadecane	250	4	8	4-methyl guaiacol	cresol	12.4	78.3	batch [64]
							4-methylcyclohexanol	16.7		
							methylcyclohexane	59.2		
Ni_2P	*h*-ZSM-5	dodecane	200	2.5	6	*m*-cresol	methyl-cyclohexane	≈100	≈91	batch [65]
Co	SBA-15	–	300	1	6	anisole	benzene	≈32	≈96	fixed-bed [67]
Co	SiO_2	–	300	1	1	guaiacol	aromatics	53.1	100	batch [26]
Co	NC	*n*-dodecane	200	2	2	eugenol	dihydroeugenol	99.1	100	batch [69]
CoN_x	NC	*n*-dodecane	200	2	2	eugenol	propylcyclohexanol	99.9	100	batch [69]
CoP_2	SiO_2	octane	300	3	6	phenol	cyclohexane	≈84	≈99	fixed-bed [71]
CoP	SiO_2	octane	300	3	6	phenol	cyclohexane	≈93	≈98	fixed-bed [71]
Co_2P	SiO_2	octane	300	3	6	phenol	cyclohexane	≈34	≈23	fixed-bed [71]
							cyclohexanol	≈66		

such as abundance and low cost compared with other transition metals.[74] Fe has been long regarded as an inactive transition metal for hydrogenation of aromatic rings,[75] therefore it exhibits great potential for the HDO of phenolics with high selectivity towards deoxygenated aromatics. In general, Fe-based catalysts could save the supply of hydrogen in HDO process, even though it is less competitive in terms of deoxygenation ratio of phenolics in HDO processes compared with other catalysts like Ni or Co containing catalysts.[73] It was reported that a higher benzene selectivity in guaiacol HDO process over Fe/C catalyst was found, compared to those exhibited over carbon supported Cu, Pd, Pt and Ru catalysts.[76] These results was further supported by a DFT (Density Functional Theory) study which suggested that the HDO process of phenol on Fe (110) surface followed the DDO reaction pathways (Figure 4, Pathway 1).[77] Tan *et al.*[78] attributed the direct cleavage of C–O bonds over Fe catalyst to the strong oxyphilicity of Fe metal. Despite the excellent catalytic results obtained with Fe-based materials (high activity and selectivity towards deoxygenated products), the main drawback of Fe is its susceptibility to get de-activated due to oxidation by surface oxygen species[79] and/or carbon deposition.[73] Hence, the investigation of Fe-based catalysts usually explores the utilization of another metal in order to overcome these major barriers leading to advanced bimetallic Fe catalysts that will be discussed later on in this review.

Mo-Based Catalysts

Minimizing the consumption of hydrogen (*i.e.* with low H_2 pressure) is one of the main concerns for upgrading of bio-oils through HDO process. High pressure is likely to produce ring saturated products via unwanted hydrogenation process thus increasing hydrogen consumption and reducing the octane numbers of the upgraded product which could hinder its direct utilization as fuel or blending with conventional oil or in the forthcoming bio-refineries.[26,80] Many efforts have been devoted to develop advanced catalysts that can perform efficient in HDO process at relatively low hydrogen pressure, producing aromatics without the saturation of benzene rings. In this regard, Mo-based catalysts show great potential for converting lignin-derived bio-oil into aromatic hydrocarbons at atmospheric pressure. For instance, unsupported β-Mo_2C was employed for vapour-phase catalytic HDO of anisole. In this report it was found that β-Mo_2C preferentially cleaved the phenolic C–O bond, instead of the weaker aliphatic C–O bond of anisole. Besides, Mo_2C catalyst was quite stable over a long period time ($t \approx 50$ h) and showed unprecedented high selectivity of benzene (>90% among C_6+ products) and high hydrogen efficiency (<9% selectivity of cyclohexane) at reaction condition of 147 °C–247 °C and ambient pressure.[81] High selectivity of aromatic hydrocarbons could also be obtained in HDO process of phenolic mixtures (*m*-cresol, anisole, 1,2-dimethoxybenzene and guaiacol) over Mo_2C catalyst, with 66% selectivity of benzene and 27% of toluene at condition of 280 °C and ambient pressure.[82] This same phenomenon of selective cleaving C_{Ar}-O bond was also observed using an unsupported MoO_3 catalyst.[83] In the HDO process of phenolics (*e.g.* phenol, *m*-cresol, anisole or guaiacol) over MoO_3 catalyst, the partially reduced MoO_3 phase (presumably Mo^{5+} state) is speculated to perform as a Lewis acid site (*i.e.* oxygen vacancy) which may weaken C–O bond upon adsorption of the reactant or intermediates on the active site. Efficient supports could obviously influence the catalytic activity of active species in Mo-based catalysts by stabilizing specific oxidation states,[84] or by influencing geometric configurations,[85] electronic properties[86] and finally prevalence of "high-energy" sites.[87] Investigation results of reactivity and stability of different supported MoO_3 catalysts (supports including SiO_2, γ-Al_2O_3, TiO_2, ZrO_2, and CeO_2) for HDO of *m*-cresol indicated that ZrO_2 and TiO_2 were optimal supports which could promote activity and improve stability of a typical MoO_3 catalyst. The selectivity of toluene derived from HDO processes over ZrO_2 and TiO_2 supported MoO_3 catalysts were greatly improved compared with unsupported MoO_3 catalyst (yielding 77% and 46% *vs* 13%). Besides, XPS analysis on spent catalysts showed that these supports can enhance the stability of MoO_3 catalysts by stabilizing Mo^{5+} species and further slowing down the deactivation process.[88] Apart from the active species and their influence of the stability/selectivity balance, the metal/support ratio could also affect the performance of the supported materials. For example, when MoO_3/ZrO_2 catalysts are considered, an increased loading of MoO_3 on ZrO_2 (from 1 wt.% to 36 wt.%) resulted in the dispersion of Mo particles varying from isolated species to oligomeric domains to crystallites of MoO_3 and $Zr(MoO_4)_2$. HDO and alkylation was favoured when the dispersion of oligomeric MoO_x species obtained at loadings approaching a monolayer coverage (≈ 5 Mo/nm^2). It is indicated that the existence of clear connection oxide loading-structural properties-catalytic performance.[89] The latest results of Mo-based catalysts for HDO of phenolic compounds in lignin-derived bio-oil performed at atmospheric pressure are listed in Table 2. Again, the fact that these catalysts are able to work at atmospheric pressure is something commendable that must be highlighted in the catalytic HDO context.

In spite of the remarkable HDO activity of Mo_2C at atmospheric pressure, it has to be mentioned that Mo_2C catalyst can be deactivated in the presence of H_2O because water tends to oxidize Mo_2C into MoO_2, which has lower HDO activity. Hence, it is crucial to remove the H_2O produced from HDO process timely. Besides, as shown on Table 2, the conversion ratio of reactant over MoO_3 catalyst is not competitive compared the other transition metals, like Ni. Efforts are needed to break the gambling relation between conversion ratio and selectivity of aromatics over Mo-based catalyst in HDO process.

2.1.1.2 Noble Metals

Noble metals, such as Pt, Pd, Ru, Rh *etc.* have been widely studied since they possess excellent catalytic properties in HDO of phenolic compounds. Generally speaking, noble metal catalysts possess higher hydrogenation activity than non-noble

Table 2. Mo-based catalyst for HDO of phenolic compounds at atmospheric pressure.

Catalysts Metal	Support	Solvent	Reaction conditions T [°C]	P [MPa]	t [h]	Model compounds	Major products	Sel. [%]	Conv. [%]	Reactor	Ref.
Mo_2C	C	–	247	0.1	≈14 ≈35	anisole	benzene (among C_6^+)	≈95 ≈95	100 100	tubular quartz	[81]
Mo_2C	C	–	280	0.1	1	*m*-cresol: anisole:1,2-dimethoxybenzene: guaiacol = 1: 0.96: 0.95: 0.98	benzene toluene cyclohexanes	66 27 5	94	tubular quartz	[82]
MoO_3	–	20 wt% mesitylene	320	0.1	3	phenol	benzene	93.7	28.7	packed bed	[83]
MoO_3	–	–	320	0.1	3	*m*-cresol	toluene	99.3	48.9	packed bed	[83]
MoO_3	–	–	320	0.1	3	anisole	benzene toluene	55.9 19.8	78.7	packed bed	[83]
MoO_3	–	–	320	0.1	3	guaiacol	benzene phenol	16.0 41.9	97.5	packed bed	[83]
MoO_3	ZrO_2	–	320	0.1	3	*m*-cresol	toluene	98.7	78	packed bed	[88]
MoO_3	TiO_2	–	320	0.1	3	*m*-cresol	toluene	97.9	47	packed bed	[88]
MoO_3	ZrO_2	–	320	0.1	0-4 (average)	anisole	benzene phenol cresol dimethyl phenol	23 18 18 13	62	packed bed	[89]

catalysts.[49a,90] Hence, noble catalysts alone are not a proper choice for producing aromatic hydrocarbons as benzene rings in reactant are tend to be saturated in HDO process.[91] However, noble metal (*i.e.* Rh, Pd and Pt) supported on less acidic support (like ZrO_2) is an effective alternative of conventional sulfided $CoMo/Al_2O_3$ catalysts in terms of high activity and excellent stability.[92] Accordingly, noble metal based catalysts are effective candidates for long-term usage in phenolics HDO process. However, the scarce resources and high cost of noble metals hinders their industrial application prospects.[93] Based on the experimental results of guaiacol HDO by using noble metals (*i.e.* Pt, Rh, Pd, Ru) supported on acidic carriers (*i.e.* Al_2O_3, SiO_2-Al_2O_3, nitric-acid-treated carbon (NAC)), the reaction pathway of HDO over acid-supported noble metal catalysts was proposed (Figure 9).[94]

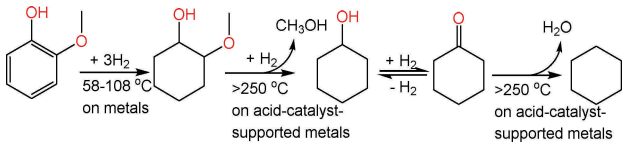

Figure 9. Proposed reaction pathways of acid-supported noble metal (Pt, Rh, Rd, Ru) catalysts in HDO of guaiacol (reprinted from [94] with permission of Elsevier. Copyright 2012 Elsevier).

Pt-Based Catalysts

Platinum (Pt)-based catalysts favour the saturation of aromatic rings or C=C bonds prior to the direct cleavage of C–O bond,[95] due to its excellent hydrogenation ability. Pt shows the highest hydrogenation ability followed by Ru and Pd.[96] Zanuttini *et al.*[97] concluded that the metal phase catalysed for the phenol deoxygenation, while transalkylation reactions such as disproportionation, isomerization, alkylation, together with condensation reactions were attributed to the acid sites in the support when anisole was used as model compound in HDO over Pt-based catalyst. However, a theoretical investigation by using DFT method and experimental results indicated that Pt (111) metallic sites were not active deoxygenation sites in HDO of guaiacol and the deoxygenation activity of Pt catalysts were speculated from the existence of catalyst support or Pt step and corner sites.[98] Hence the utilisation of a support which could favour the deoxygenation is needed to boost the overall deoxygenation capacity of Pt-based metal catalysts. The type of support can greatly influence the reactivity of Pt-based catalyst. A recent study showed that the reactivity order of Pt-based catalysts with different supports followed the order as: $Pt/SiO_2 > Pt/Al_2O_3 \approx Pt/ZrO_2 > Pt/P25 > Pt/TiO_2 \approx Pt/ZrO_2$mono $\approx Pt/CeO_2$.[50] In contrast, Pt supported on the acidic carriers like H-MFI zeolites presented the highest activity (conversion: 100%, selectivity of cyclohexane: 93%) at 180 °C and 5 MPa of H_2, suggesting the acidity of the support played an significant role in the deoxygenation of the methoxy group in guaiacol.[50] Pt supported on microporous zeolites, HY, were used as bifunctional catalysts for HDO of phenolic compounds (guaiacol, anisole and phenol). It was reported that the yield of major product, cyclohexane, increased with the increasing number of acid sites in catalyst. HDO process of anisole over Pt/HY catalysts can achieve high conversion and selectivity ratio of cyclohexane (both > 90%) at 250 °C and 4 MPa.[99] The effect of zeolitic support on the activity of Pt-based catalysts can be seen from Lee and co-workers' investigation. They loaded Pt on six types of zeolitic materials, namely Pt/Meso Beta, Pt/HZSM-5, Pt/

HBeta, Pt/MMZBeta, Pt/Si-MCM-48 and Pt/Al-MCM-48, and further investigated their activities in HDO of guaiacol at 250 °C and 4 MPa. Results showed that compared to other Pt-based bifunctional catalysts, Pt/Meso Beta and Pt/HBeta, which exhibited both large pores and strong acid sites, showed higher conversion ratio of guaiacol (>90%).[100] It can be concluded that sufficiently large pores and sufficient quantity of acid sites are all indispensable for effective conversion of phenolics in HDO process using Pt-based catalysts. However, bifunctional Pt-based catalyst (Pt/acidic zeolite or Pt/Al_2O_3) showed less stability compared with Pt supported inert matrices (Pt/SiO_2 or Pt/TiO_2) due to the severe coke formation during HDO process.[42,100–101] The later indicates the need to establish a fair balance between cracking and hydrogenation to successfully design Pt-based catalysts for HDO reactions.

Pd-Based Catalysts

Palladium (Pd), with more abundant reserves and a lower cost than Pt[102] is also known due to its high hydrogenation activity in numerous hydrogenation process.[103] Pd dispersed on inert support (*i.e.* carbon nitrides (CN) or mesoporous silica (KIT-6)) results fairly effective for partial deoxygenation of phenolic compounds with high selectivity of specific products.[104] For example, mesoporous carbon nitride-supported Pd catalyst was effective for cleaving C=O and well protecting the C_{Ar}–OH and C_{Ar}–OCH_3 in vanillin at moderate reaction condition (50 °C and 0.1 MPa), achieving 100% selectivity of 2-methoxy-4-methylphenol (MMP) in fully conversion. The Pd@CN also showed superior HDO activity compared commercially Pd@C and other typical oxide-supported Pd catalyst (*e.g.* $Pd@TiO_2$, Pd@MgO, $Pd@CeO_2$ and $Pd@Al_2O_3$) under the same reaction condition. It is known that doping N atoms in carbon structure could increase the hydrophilic property of catalyst. Hence, it is speculated that the effect of N favoured the catalyst dispersion in water and enhance the exposure of catalyst to substrate, thereby increasing the catalytic performance significantly.[104a] The superior HDO activity of Pd@CN indicated N-doped carbon support is an advisable choice for the transformation of carbonyl group(–CHO) into methyl group (–CH_3) in aqueous media.[104b] In contrast, Pd/KIT-6 catalyst was effective for cleave both C=O and C-OCH_3 and well protects O–H bond, showing 98% conversion of vanillin and 94% selectivity of *p*-cresol at 300 °C for 6 h.[104c] Lu *et al.*[105] investigated the hydrogenation of guaiacol over Pd catalyst on different titania and carbon supports. Compared to carbon supported catalyst, the titania supported catalyst showed a higher C–O bond scission ability. It was speculated that the adsorption and cleavage of C–O bond in hydrogenation product (2-methoxylcyclohexanol) mainly occur on the partially reduced titanium species stemming from the reduction of Ti^{4+} by spillover hydrogen from Pd. The more partially reduced titanium species in Pd/TiO_2 catalyst, the higher the HDO activity of guaiacol among the Pd catalysts supported on three types of TiO_2 (anatase, rutile, and P25). Considering the high hydrogenation activity of Pd, the addition of acidic supports was essential to obtain the target of removing oxygen atoms in HDO process. Hierarchical ZSM-5 zeolites have been used as support for Pd catalyst. In particular, Pd/*h*-ZSM-5(30) exhibited excellent activity and selectivity (conversion: 100%, selectivity: 99%) for *m*-cresol HDO to methylcyclohexane. Results indicated that it is a facile means to improve the performance of catalyst in HDO process by tailoring the pore architecture of solid acids.[47]

Ru-Based Catalysts

Similar to Pt, ruthenium (Ru) also presents high hydrogenation activity.[106] Ru showed the highest ring-opening activity compared with Pt and Pd catalysts as evidenced by 100% yield of gas-phase products in guaiacol HDO process at relatively high temperature (350 °C).[76] Theoretical studies by DFT calculation showed that metallic Ru surface preferentially catalysed the saturation of benzene rings in phenolic compounds, and the direct scission of C–O bond was very unlikely to happen.[107] The investigations of Ru-based catalysts have mainly focused on the effect of support on adjusting the distribution of products in HDO of phenolic compounds. Phan *et al.*[108] investigated the catalytic HDO process of anisole by using Ru-based catalysts with different nanocrystalline mesoporous supports (TiO_2, Al_2O_3, SBA-15 and P25). It was evidenced that both Ru particle size and catalytic activity varies with the type of support. Ru metal exhibited the smallest particle size when supported on meso-TiO_2 support and a higher conversion ratio and benzene yield was observed in HDO process of anisole over this catalyst. HDO reaction pathways over Ru/meso-TiO_2 and Ru/P25 followed the direct deoxygenation (DDO) route (Figure 10) to produce benzene. It can be attributed to the deficient Ti^{3+} sites or oxygen vacancies.

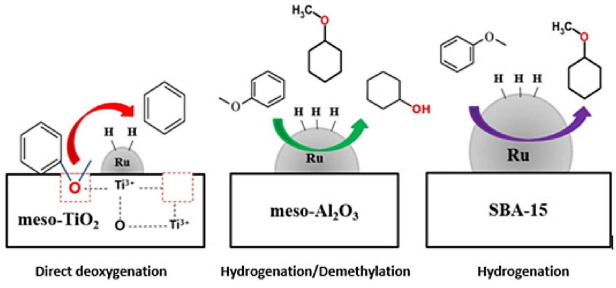

Figure 10. Hydrogenation mechanism for anisole depending on the particle size (reprinted from ref. [108] with permission of Elsevier. Copyright 2017 Elsevier).

Moreover, the same study revealed that the phase and mesoporous structure of TiO_2 played a crucial role in enhancing its interaction with metal particles and also in selecting the reaction routes of HDO reaction.[108] The excellent Ru/TiO_2 can also be seen in the phenol HDO process. It was speculated that the high activity of Ru/TiO_2 catalyst superior to other Ru-based catalysts (*i.e.* Ru/Al_2O_3, Ru/C and Ru/SiO_2) could be attributed to its redox reactivity and enhanced hydrogen spillover, which

favoured a strong interaction with the oxygen to facilitate the cleavage of C–O bond.[109] The catalytic activities of Ru nanoparticles loading on different carbon materials (multi-walled carbon nanotubes (MWCNT), carbon aerogel (CARF), carbon black (Vulcan carbon), activated carbon (AC), and graphite were investigated by Dwiatmoko and co-workers.[110] Results indicated that Ru/MWCNT exhibited the highest deoxygenation ratio (81.6%) with guaiacol conversion of 98.1% in HDO process, while Ru/AC and Ru/CARF showed lower deoxygenation ratio even though they exhibited a larger Ru dispersion together with more oxygen-containing functional groups on the supports. The activity of carbon supported catalyst is speculated be determined by the pore structures of catalyst as acid properties of carbon surfaces are not apparently different among these carbon supports. The higher ratio of mesopore to micropore surface areas of MWCNT, which could lead to better accessible of the reactant to Ru, explained the superior activity of Ru/MWCNT. Selective cleavage of C_{aryl}-OCH_3 bond of guaiacol for producing cyclohexanol and methanol can be achieved over Ru/C catalyst with MgO. It is speculated that the present of base (MgO) could be suppressed the unselective C–O cleavage by Ru catalyst and enhance the demethoxylation step by stabilizing the intermediates (*e.g.* phenol).[111]

More complex supports based on mixed oxides combinations (*i.e.* WO_x-ZrO_2,[112] TiO_2-ZrO_2,[113] ZrO_2-$La(OH)_3$[114]) have gained interest as carrier of Ru nanoparticles. For instance, Ru/WO_x-ZrO_2 (with 10 wt.% W) prepared by hydrothermal impregnation showed high conversion ratio of guaiacol (96.8%) and high percentage of non-oxygenated products (56.6%) (including cyclopentane, methylcyclopentane, and cyclohexane) in upgraded bio-oil. The fraction of W could modify the acidity and the dispersion of Ru in the catalyst and further affects the activity of HDO process.[112] TiO_2-ZrO_2 synthesized via deposition-precipitation method was also applied as support for Ru-based catalysts. Ru/TiO_2–ZrO_2 catalyst was effective for the production of benzene (conversion: ≈100%, selectivity: ≈45%) in guaiacol HDO process at 260 °C. The presence of ZrO_2 in the support greatly improved the activity of Ru catalysts since ZrO_2 hinders the migration of Ti^{3+} species which was said to cover the surface of metal particles blocking the accessibility of the reactants to the active sites.[113] As indicated by Xu *et al.* the catalytic activity of Ru based catalysts for the conversion of guaiacol (200–260 °C) followed the order: Ru/TiO_2-ZrO_2 (1:3)≥ Ru/TiO_2–ZrO_2 (1:1)≈Ru/TiO_2–ZrO_2 (3:1)> Ru/TiO_2>Ru/ZrO_2. Ru supported on ZrO_2–$La(OH)_3$ was effective for partial deoxygenation of guaiacol, which presented excellent activity of removing a methoxyl group (C-OCH_3) and maintaining a hydroxyl group (-OH), leading to the selective production of cyclohexanols with high product yields (88% yield at 200 °C).[114]

Rh-Based Catalysts

Rhodium (Rh) is one of the rarest and most expensive metals.[115] For this very reason only few experimental studies investigated the HDO of phenolic compounds over Rh-based catalyst. It should be mentioned that theoretical studies indicate great potential of Rh for the HDO process. When comparing model surfaces, the C–O bond breakage of phenol and cyclohexanol over Rh (111) and Rh (211) surfaces using DFT it was demonstrated that the ability of cleave C–O bond over Rh (211) was more efficient than that of Rh (111). Results indicated that phenol will mainly react via a pathway of initial hydrogenation followed by deoxygenation to produce the final deoxygenated product, cyclohexane.[116] The initial hydrogenation pathway was favoured by the experimental study of guaiacol HDO over Rh/ZrO2.[117] Different types of zeolites with MWW framework including MCM-22(C), MCM-22(SC) and MCM-36, were used as support in bifunctional Rh-based catalysts. Comparatively, Rh nanoparticles supported on the MCM-36 exhibited the highest activity in guaiacol HDO process, mainly resulted from the higher metal dispersion and acid sites population on the external surface.[118] The investigation of catalysts stability is very important for the implementation of the catalysts in the chemical industry. Rh/SiO_2 (JM) (supplied by Johnson Matthey) showed better stability than Rh/SiO_2 (A) (prepared in-house) with a stable activity over 3 days of reaction in HDO of *p*-methylguaiacol, while higher coking was observed on commercial catalysts. This apparent contradiction suggested that there was no direct link between carbon deposits and catalyst deactivation for these noble metal/silica catalysts.[119] Perhaps deeper understanding of the deactivation phenomena (*i.e.* type of carbon, metallic sintering, preservation of textural properties, etc.) should be further investigated to complement the study on ref. [119].

Other Noble Metal-Based Catalysts

Noble metal, like gold (Au) and rhenium (Re), received little interest for the study of HDO of phenolics by the catalysis community due to their elevated cost which creates reservations when industrial scale applications are intended. In any case, some interesting results have been gathered using Au/TiO_2 catalysts applied to guaiacol HDO process. Au-containing catalysts showed higher selectivity of phenol (66.9%) compared with Rh/SiO_2 catalyst at 280 °C and 4 MPa of H_2.[120] On the other hand rhenium compounds such as ReS_2 has been successfully used in HDO of phenolic compounds. For example, ReS_2 supported on activated carbon (AC) favoured the formation of partial deoxygenation products, such as phenol.[121] In contrast, ReO_x loading on carbon nanofiber (CNF) support exhibited a strong affinity for direct breakage of the C–O bond to produce benzene (selectivity: 30.2%) in anisole HDO process at 300 °C and 5 MPa.[122]

As a matter of summary of the capabilities and application of monometallic noble metal formulations in HDO, Table 3 represents an overview of the reviewed literature. Overall, noble metal-based catalysts display promising skills for their direct application in catalytic HDO processes. Most of them are very active and selective although sometimes their advanced activity in hydrogenation could influence (negatively) on the selectivity making necessary to adjust their catalytic functions by playing with the support composition or using promoters. Also, the

Table 3. Noble metal (Pt, Pd, Ru, Rh, Au and Re)-based catalysts for HDO of phenolic compounds.

Catalysts		Solvent	Reaction conditions			Model compounds	Major products	Sel. [%]	Conv. [%]	Reactor	Ref.
Metal	Support		T [°C]	P [MPa]	t [h]						
Pt	SiO_2	*n*-hexadecane	180	5	5	guaiacol	cyclohexane methoxycyclohexane cyclohexanol methoxycyclohexanol	8 10 20 51	86	batch	[50]
Pt	H-MFI-90	*n*-hexadecane	180	5	5	guaiacol	cyclohexane	93	100	batch	[50]
Pt	HY	decane	250	4	2	guaiacol	cyclohexane	≈57	≈94	batch	[99]
Pt	HY	decane	250	4	2	anisole	cyclohexane	≈92	≈91	batch	[99]
Pt	HY	decane	250	4	2	phenol	cyclohexane	≈70	≈96	batch	[99]
Pt	HZSM-5	decane	250	4	3	guaiacol	-	-	15	batch	[100]
Pt	mesoporous Beta	decane	250	4	3	guaiacol	cyclohexane cyclopentane, methyl-	≈26.9 ≈13.5	≈97	batch	[100]
Pt	HBeta	decane	250	4	3	guaiacol	cyclohexane cyclopentane, methyl-	≈45.7 ≈15.4	≈99	batch	[100]
Pt	MMZBeta	decane	250	4	3	guaiacol	cyclohexane	≈70.4	34	batch	[100]
Pt	Al-MCM-48	decane	250	4	3	guaiacol	cyclohexane	≈58.5	64	batch	[100]
Pt	Si-MCM-48	decane	250	4	3	guaiacol	1,2-dimethoxy benzene	≈11	≈3	batch	[100]
Pd	CN	water	90	0.1	0.5	vanillin	2-methoxy-4-methylphenol (MMP)	100	100	flask	[104a]
Pd	CN	water	50	1	7	vanillin	MMP	99	99	batch	[104b]
Pd	mesoporous KIT-6	methanol	300	0.1	6	vanillin	*p*-cresol	94	98	fixed-bed	[104c]
Pd	TiO_2 (anatase)	*n*-dodecane	260	3	6	guaiacol	cyclohexane	≈70	≈100	fixed-bed	[105]
Pd	*h*-ZSM-5(30)	*n*-dodecane	200	2	6	*m*-cresol	methylcyclohexane	99	100	batch	[47]
Ru	mesoporous TiO_2	–	200	30	3	anisole	methoxy-cyclohexane cyclohexane benzene	64.6 26.8 4.1	100	batch	[108]
Ru	(nonporous conventional TiO_2) P25	–	200	30	3	anisole	methoxy-cyclohexane cyclohexane cyclohexanol	35.3 32.5 28.6	100	batch	[108]
Ru	mesoporous Al_2O_3	–	200	30	3	anisole	cyclohexane methoxy-cyclohexane cyclohexanol benzene	46.5 24.3 21 2.6	100	batch	[108]
Ru	mesoporous Silica (SBA-15)	–	200	30	3	anisole	cyclohexane methoxy-cyclohexane cyclohexanol	55.6 21.4 10.8	100	batch	[108]
Ru	MWCNT	water	270	4	1	guaiacol	-	81.6[a]	98.1	batch	[110]
Ru	CARF	water	270	4	1	guaiacol	-	48.0[a]	81.7	batch	[110]
Ru	Vulcan carbon	water	270	4	1	guaiacol	-	52.9[a]	77.0	batch	[110]
Ru	AC	water	270	4	1	guaiacol	-	65.6[a]	96.1	batch	[110]
Ru	graphite	water	270	4	1	guaiacol	-	5.7[a]	14.6	batch	[110]
Ru	C (with MgO as base)	water	160	1.5	2	guaiacol	cyclohexanol	79[b]	98	batch	[111]
Ru	WO_x-ZrO_2	water	270	4	1	guaiacol	cyclopentane methylcyclopentane cyclohexane	56.6	96.8	batch	[112]
Ru	TiO_2-ZrO_2	*n*-dodecane	260	2	6	guaiacol	benzene cyclohexane	≈45 ≈32	≈100	fixed-bed	[113]
Ru	ZrO_2-$La(OH)_2$	water	200	4	4	guaiacol	cyclohexanol 2-methoxy cyclohexanol cyclohexane	91.6 5.8 1.3	100	batch	[114]
Rh	ZrO_2	-	400	5	1	guaiacol	cyclohexane	≈42	100	Pyrex reactor	[117]
Rh	MCM-22(C) [c]	*n*-decane	250	4	1.3	guaiacol	–	2.9[e]	66	batch	[118]
Rh	MCM-22(SC) [d]	*n*-decane	250	4	1.3	guaiacol	–	6.3[e]	61	batch	[118]
Rh	MCM-36	*n*-decane	250	4	1.3	guaiacol	–	3.3[e]	69	batch	[118]
Rh	SiO_2 (JM)	–	300	0.4	1	*p*-methylguaiacol	*m*-cresol *p*-cresol 4-methycatechol	≈18 ≈55 ≈6	-	fixed-bed	[119]
Rh	SiO_2 (JM)	–	300	0.4	32	*p*-methylguaiacol	*m*-cresol *p*-cresol 4-methycatechol	≈18 ≈55 ≈11	-	fixed-bed	[119]
Rh	SiO_2 (A)	–	300	0.4	1	*p*-methylguaiacol	toluene *m*-cresol *p*-cresol 4-methycatechol	≈33 ≈13 ≈30 ≈3	-	fixed-bed	[119]
Rh	SiO_2 (A)	–	300	0.4	32	*p*-methylguaiacol	toluene *m*-cresol *p*-cresol	≈2 ≈10 ≈35	-	fixed-bed	[119]

Table 3. continued

Catalysts		Solvent	Reaction conditions			Model compounds	Major products	Sel. [%]	Conv. [%]	Reactor	Ref.
Metal	Support		T [°C]	P [MPa]	t [h]						
							4-methycatechol	≈42			
Au	TiO_2	–	280	4	1	guaiacol	phenol	66.9	57.8	continuous flow	[120]
							cresols	9.1			
ReS_2	GAC active carbon	dodecane	300	5	4	guaiacol	phenol	≈80	≈97	batch	[121]
							catechol	≈5			
ReO_x	CNF_{ox}[f]	dodecane	300	5	4	guaiacol	cyclohexane	66.1	100	batch	[122]
							benzene	19			
							phenol	7.9			
ReO_x	CNF_{ox}[f]	dodecane	300	5	4	anisole	cyclohexane	52.7	88.1	batch	[122]
							benzene	30.2			
ReO_x	CNF_{ox}[f]	dodecane	300	5	4	phenol	cyclohexane	82.4	100	batch	[122]
							benzene	17.6			

[a] Oxygen removal ratio; [b] Calculated based on the number of C_6 rings; [c] MCM-22 (C): three-dimensional MWW type zeolites converted from a layer-structured MCM-22 (P: precursor) with interlayers; [d] MCM-22 (SC): MCM-22 (SC: swollen and calcined); [e] oxygen removal percentage; [f] oxidized carbon nanofiber.

catalysts stability although superior to that exhibited by base metals (*i.e.* Ni), it is not always satisfactory. These limitations along with their market price make them a less preferable option and challenge the catalysis community to search highly efficient noble metal-free catalysts.

2.1.2 Bimetallic Catalysts

Compared with monometallic catalyst, the application of bimetallic catalysts is an effective method since it possesses the possibility to enhance the selectivity to particular products by the interaction between the metals to modify the geometric and electronic structures of the metal surface.[123] It is promising catalytic formulation for achieving high catalytic activity which could perform under relatively mild reaction conditions and with less hydrogen consumption compared with the condition of monometallic systems. Some authors coincide on their conclusions claiming that the improvement of HDO activity over bimetallic catalysts seems to be linked to the enhancement of demethoxylation and deoxygenation pathways.[33b,124] For example, NiCo bimetallic catalytic system[68,125] has been widely studied for upgrading lignin-derived bio-oil or phenolic compounds. The performance of NiCo bimetallic catalysts was better than that of monometallic Ni and Co catalyst, which could be attributed to the present of Ni–Co alloy resulting in the increased dispersion and stability of Ni active phase.[125a] Similarly, other alternatives like NiPd,[126] PtCo,[127] NiCu[128] *etc.* exhibited an improvement in terms of HDO activity compared with their monometallic counterparts. However, generally, high deoxygenation degree could only be obtained with the present of acidic sites, usually provided by the support, in these catalytic systems.

2.1.2.1 Catalyst with Oxyphilic Metal

Bimetallic catalytic system engineered as a combination of noble metals (*i.e.* Ru, Pd, Pt) or base metals (*i.e.* Ni) with oxyphilic metals (*i.e.* Fe, Re, Mo) is an effective strategy for improving the HDO activity and adjust the products distribution. Typically, the induction of oxyphilic metals could improve HDO activity without the use of acidic supports. This strategy have an apparent advantage over metal-acid support catalyst without the drawbacks associated with the use of acidic support, which could promote the side reactions in HDO of bio-oil, such as polymerization.[16] Besides strong acidity can induce a higher rate of coke formation, leading to fast deactivation of catalysts.[16]

Fe-Contained Bimetallic Catalysts

It was reported that the addition of Fe to the Ru/meso-TiO_2 catalyst can drastically change the reaction pathways from HYD to DDO, resulting a high selectivity of benzene (selectivity: >80%) in HDO of anisole at 250 °C and 1 MPa of H_2. In RuFe/meso-TiO_2 catalyst, Ru particles dissociated H_2 while the oxyphilic Fe sites enhanced the interaction between oxygen-containing compounds and the surface of TiO_2 support (Figure 11). The enhanced activity of bimetallic RuFe catalyst seems to be linked to the increased number of oxygen vacancies on the surface of support.[129] Similarly, bimetallic PdFe/C also favoured the DDO reaction pathways in which the catalytic activity and selectivity of aromatic compounds were significantly enhanced in guaiacol HDO process obtaining 83.2% yield to deoxygenated products (including benzene, toluene and trimethylbenzene), opposed to the 43.3% yield obtained with a monometallic Fe/C at 450 °C.[76] A kinetic study of Pd–Fe catalyst used in HDO of *m*-cresol in the present of water showed that Pd provided an enhanced reaction pathway at the Pd–Fe interface which resulted in the promoted catalysis on Fe without changing the primary reaction mechanism of direct

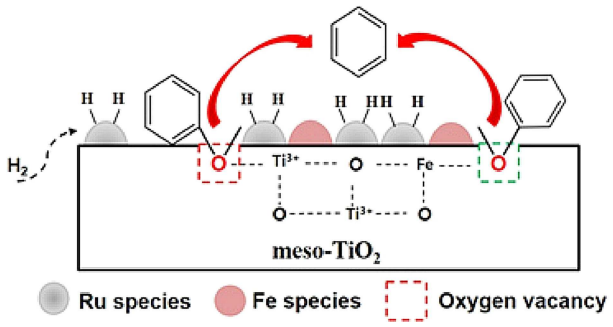

Figure 11. Reaction mechanism for the HDO of anisole over $RuFe/TiO_2$ catalyst (reprinted from [129] with permission of Elsevier. Copyright: 2018 Elsevier).

C–O cleavage reaction pathway.[130] Further Pd–Fe synergy was found by the investigation about the function of the surface of Pd in the reduction process of Pd/Fe_2O_3 catalyst. In innovative system, Pd atoms protected Fe from oxidation due to this the enhanced reducibility and promotion of water formation on the mixed material as demonstrated both theoretical and experimentally.[131] The combination of Fe and Ni results in high activity and significant selectivity improvement to cyclohexane or phenol by varying the Ni/Fe ratios compared with monometallic Ni or Fe catalysts. Characterization results showed that Ni–Fe alloys were found in the bimetallic catalysts leading to synergistic effects that boost the overall catalytic performance. Briefly, Ni promoted the dissociation of H_2, while Fe played a significant role in oxygen affinity.[132] The different reaction routes of guaiacol HDO over Ni–Fe and Pd–Fe bimetallic were presented in Figure 12.[76,132]

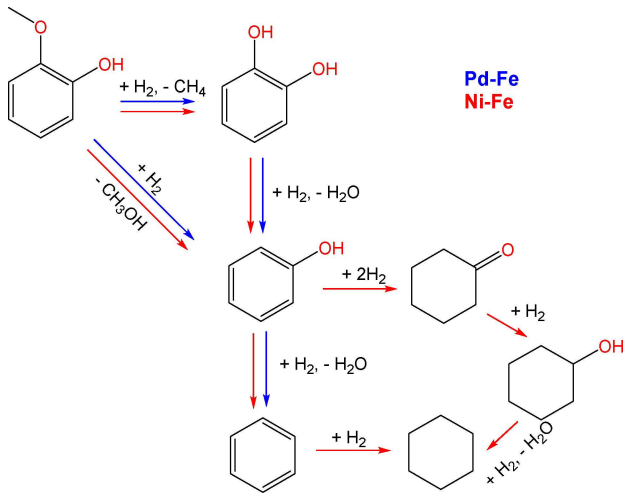

Figure 12. Main reaction routes over bimetallic Pd–Fe/C and Ni–Fe/CNTs catalysts in guaiacol HDO process (adopted from ref. [76,132])

Re-Contained Bimetallic Catalysts

A kinetic study and DFT calculation showed that NiRe bimetallic catalyst exhibited both geometric and electronic effect for converting *m*-cresol to toluene through HDO process. The function of Re could be summarized as: (1) Re decreased Ni particle size and stabilized the highly dispersed NiO, resulting from the strong interactions of Ni–O–Re; (2) the proximity between Ni and Re reduced the *d*-bond occupancy of Ni, resulting in the reduced popularity of the phenyl rings adsorption on the surface which prevented the C–C hydrogenolysis of aromatics.[133] Fukuoka *et al.*[134] investigated catalytic performance of Ni/ZrO_2 and Pt/ZrO_2 catalysts with the addition of Re for converting lignin model compounds 4-propylphenol into *n*-propylbenzene through HDO process in the presence of water. Reaction pathways of 4-propylphenol HDO over PtRe and NiRe catalysts was presented in Figure 13.

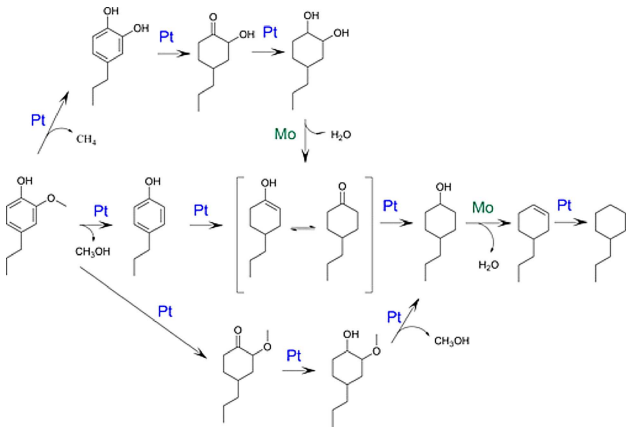

Figure 13. Proposed reaction routes over ZrO_2 supported PtRe and NiRe bimetallic catalyst in HDO of 4-propylphenol (adopted from ref. [134]).

Reaction pathways in this bimetallic catalytic system was quite different from the typical HDO mechanism of phenols (Figure 4). The activity of $PtRe/ZrO_2$ catalyst was superior to that of $NiRe/ZrO_2$ in terms of the production of *n*-propylbenzene (maximum selectivity of 80% *vs* 54%). Jung *et al.*[135] investigated the effect of carbon support on the HDO of guaiacol over RuRe catalyst. Results showed that ReRu/MWCNT and ReRu/VC displayed a significantly enhanced activity and hydrocarbons selectivity for HDO of phenolic compounds (*i.e.* guaiacol, eugenol, benzyl phenyl ether) compared to ReRu/AC. The inferior performance of AC-supported catalyst was attributed to the hindered assembly of Re and Ru due to the high microporosity and high surface oxygen functionalities of AC surface restrict the mobility of active metal particles.

Mo-Contained Bimetallic Catalysts

It was reported that the *m*-cresol underwent entire HDO to produce high percentage of methylcyclohexane (MCH) (selectiv-

ity: ≈70%) over PtMo catalyst (with C support) in the absence of an acidic support materials, while the MCH formation was quite slow over monometallic Pt-based catalyst. Experimental results and DFT calculation indicated that Mo sites on the surface of PtMo significantly lower the energy barrier for *m*-cresol tautomerization and subsequent deoxygenation process, resulting the introduction of tautomerization-deoxygenation pathway for PtMo catalyst in contrast to the ring hydrogenation pathway over Pt catalyst.[46a] PtMo/MWCNT catalyst employed in HDO of dihydroeugenol, a more complicate lignin-derived monomers, showed high activity, with unprecedented high yield of hydrocarbon propylcyclohexane (yield ≈98%).[136] The reaction pathways in PtMo/MWCNT catalytic system is presented in Figure 14. The novel feature of PtMo catalyst system

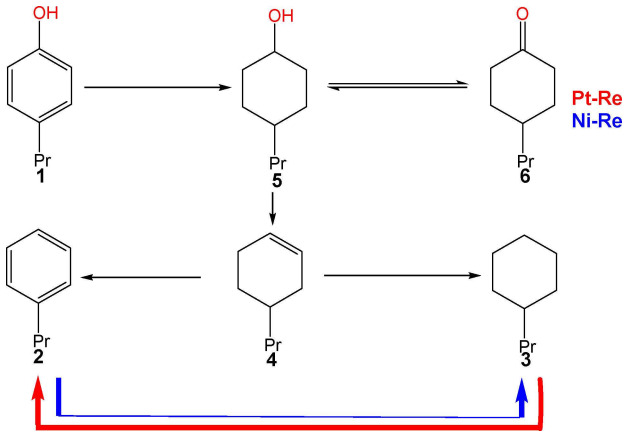

Figure 14. Proposed HDO reaction pathway for the high pressure conversion of lignin-derived model compound dihydroeugenol over bimetallic PtMo/MWCNT catalyst (reprinted from ref. [136] with permission of Elsevier. Copyright: 2016 Elsevier).

was the ability of Mo-containing phase to conduct dehydration reactions as seen on other "traditional acid" catalysts. Overlayer catalysts are popular attempts of advanced HDO catalysts. For instance, Lai *et al.*[137] prepared SiO_2-Al_2O_3 supported double deposition Mo@Pt (DD) and single deposition Mo@Pt (SD) overlayer catalysts via directed deposition technique and employed in HDO of guaiacol and anisole to investigate the selectivity of aromatic hydrocarbons, BTX (benzene, toluene and xylenes). Characteristic studies have indicated that platinum might be deposited atop the supported molybdenum parent catalyst. Mo@Pt (DD) showed the highest selectivity of BTX for guaiacol and anisole HDO process (selectivity: 84% and 81%, respectively) improving substantial performance of monometallic Pt or Mo catalyst. Tran *et al.* investigated the HDO activity of guaiacol over Mo contained bimetallic sulfide catalyst supported on mesoporous SiO_2. It was interesting to find that with an addition of tungsten (W) to bimetallic sulfided catalysts, the activity was greatly improved in terms of the content of unconverted oxygen. The deoxygenation activities of catalysts followed the order: NiMoW > NiMo > CoMo/Al_2O_3 > NiMoW bulk > CoMo.[138]

2.1.2.2 Catalyst with Alkali Metals

Introducing dopants in catalysts' formulations is another strategy to alleviate the deactivation drawbacks, especially for that of metal-acid catalyst. Alkali metals, such as Na and K can act as acidity modifiers though the interaction with acid support. It was reported that K could act as an acidity modifier in CoMo/γ-Al_2O_3 catalysts which aids to resist the deactivation process. It is speculated that formation of a basic [≡Al–OH]–K^+ surface complex resulted in an overall acidity depletion of catalyst.[139] The addition of small amounts of K to NiMo/Al_2O_3 and CoMo/Al_2O_3 sulfided catalysts resulted in an increase in the yields to the desired products and stronger resistance to coking. The selectivity shifting from demethylation and methyl substitution reactions to direct C_{Ar}–OH bond cleavage and hydrogenation reactions was driven by the promoter effect.[140] A brief overview of the reviewed literature on bimetallic systems is depicted in Table 4.

In summary, the bimetallic strategy helps to developed suitable catalysts for HDO reactions. Their benefits are multiple including synergistic effects, greater tolerance to deactivation and higher selectivity towards saturated oxygen-free products. The preparation route is essential to achieve advanced catalytic properties and examples of unsuccessful bimetallic catalysts (compared to monometallic) are frequent in literature. The combination of noble metal and oxyphilic metal in bimetallic formulation is a promising strategy for avoiding the use of acid supports. Furthermore, the addition of promoter and in particular alkaline species such as K is an interesting approach to further boost the catalytic skills of leading to highly effective multicomponent HDO materials.

2.2 Solvent's Effect

HDO research on phenolic compounds is mainly conducted in oil phase system, such as hexadecane,[141] decalin,[40a,142] decane,[94,99–100] octanol,[101,143] and dodecane[144] considering the high solubility of reactants in these organic solvents. However, some investigations also attempt to employ water[25b,125a, 145] or even aqueous-oil and bi-phasic solvents.[146] We should keep in mind that bio-oil is a complex liquid mixture (with a big fraction of phenolic compounds) containing two immiscible phases (aqueous and organic). The diffusion limitations of reactants, intermediates and even products within the solvent could apparently reduce the activity and selectivity of the used catalysts in HDO process.[146b,147] Nevertheless, the effect of solvent on the reaction mechanism and productivity has often been neglected compared with the study of catalysts and reaction parameters (*i.e.* reaction temperature, H_2 partial pressure and reaction time) in the HDO process. Although this review is mainly focused on catalyst design and strategies for the development of advanced HDO catalysts we believe that some notions about solvent influence should are beneficial at this point. Indeed, solvent effects must not be ignored since chemical reactions are influenced by the integrated interactions among solvent, catalyst, reactants and products. Such inter-

Table 4. Bimetallic catalysts for HDO of phenolic compounds.

Catalysts		Solvent	Reaction conditions			Model compounds	Major products	Sel. [%]	Conv. [%]	Reactor	Ref.
Metal	Support		T [°C]	P_{H2} [MPa]	t [h]						
Ru-1Fe	meso- TiO_2	decane	250	1	3	anisole	benzene cyclohexane methoxycyclohexane	≈84 ≈7 ≈2	≈98	batch	[129]
2Pd-10Fe	C	–	450	0.04	1	guaiacol	benzene + toluene + trimethylbenzene	≈83	≈100	fixed-bed	[76]
5Ni-1Fe	carbon nanotubes (CNTs)	–	400	3	2	guaiacol	cyclohexane	83.4	96.8	fixed-bed	[132]
1Ni-5Fe	CNTs	–	400	3	2	guaiacol	cyclohexane phenol	2.5 83.3	47.2	fixed-bed	[132]
Pt-Re	ZrO_2	water	280	2	1	4-propylphenol	*n*-propylbenzene	≈80	91	batch	[134a]
Ni-Re	ZrO_2	water	300	4	1	4-propylphenol	*n*-propylbenzene	54	100	batch	[134b]
Ru-Re	MWCNT	*n*-heptane	240	2	1	guaiacol	cyclohexane	≈80	100	batch	[135]
Ru-Re	VC (Vulcan carbon)	*n*-heptane	240	2	1	guaiacol	cyclohexane	≈85	100	batch	[135]
1Pt-1Mo	C	–	250	0.5	-	m-cresol	methylcyclohexane (MCH)	≈70	≈100	fixed-bed	[46a]
5Pt-2.5Mo	MWCNT	–	300	38	-	dihydroeugenol (2-methoxy-4-propylphenol)	propylcyclohexane	≈97.8	≈100	fixed-bed	[136]
Mo@Pt overlayer (DD)	SiO_2-Al_2O_3	heptane	450	0.1013	1	anisole	BTX (benzene + toluene + xylenes)	81	≈99	fixed-bed	[137]
Mo@Pt overlayer (SD)	SiO_2-Al_2O_3	heptane	450	0.1013	1	guaiacol	BTX	84	≈98	fixed-bed	[137]
CoMo	–	–	400	2.8	6–8	guaiacol	hydrocarbon phenol cresol catechol	15.7 23.9 18.3 40.2	88.5	fixed-bed	[138]
NiMo	–	–	400	2.8	6-8	guaiacol	hydrocarbon phenol cresol catechol	7.6 55.3 29.5 5.1	99.9	fixed-bed	[138]
NiMoW	–	–	400	2.8	6–8	guaiacol	hydrocarbon phenol cresol catechol	27.3 43.2 17.3 9.5	99.6	fixed-bed	[138]
NiMoW bulk	–	–	400	2.8	6–8	guaiacol	hydrocarbon phenol cresol catechol	8.0 19.3 19.6 50.3	98.9	fixed-bed	[138]
CoMo	Al_2O_3	–	250	5.5	4.2	guaiacol	phenol cresol benzene catechol toluene	≈55 ≈13 ≈13 ≈7 ≈7	≈100	batch	[140]
CoMo	K-Al_2O_3	–	250	5.5	4.2	guaiacol	phenol cyclohexane catechol	≈78 ≈7 ≈6	≈68	batch	[140]
NiMo	Al_2O_3	–	250	5.5	4.2	guaiacol	catechol phenol cyclohexane cresol	≈47 ≈21 ≈12 ≈12	≈90	batch	[140]
NiMo	K-Al_2O_3	–	250	5.5	4.2	guaiacol	catechol cyclohexane phenol	≈52 ≈24 ≈21	≈87	batch	[140]

actions can trigger promotion or inhibition effects. In general, the reaction is accelerated when the promotion effect is stronger than the inhibition one and vice versa.[148] For multiple reasons, the effect of solvent in HDO process deserves much more attention:(1) some type of solvents (like water or alcohols) could be presented in bio-oil mixtures.[149] The influence of such solvents on the reaction is important for understanding the specific reaction mechanism in bio-oil upgrading processes through HDO approach; (2) properties of solvent (*i.e.* polarity and reactivity) can greatly influence the solubility of the reactants, (oxygenated molecules and H_2) as well as the stability of catalyst.[150] An adequate solvent could enhance the overall efficiency of HDO process and therefore the careful selection of the solvent is key in the overall HDO performance. Regarding the role of the solvent in HDO process in the presence of H_2, three main functions should be pointed out as follow: (1) Dissolving reactant. Solvents are essential for feeding crystalline (or solid) reactant, like phenol, in continuous HDO process.[151]

Typically, high solubility could be achieved as solvent and reactant own consistent polarity; (2) Serving as reaction medium. Solvent provides the adequate environment to facilitate the interaction between reactants and catalysts. This function is mainly found in liquid-phase HDO batch reactor set-ups which are rather common for catalytic screening;[26] (3) Acting as co-reactant. Solvents could participate in HDO reaction through interaction with reactants, catalyst or themselves,[150c,152] which is commonly found when polar protic solvents are employed.

Solvents can be classified into three categories according to the polarity, including polar protic, polar aprotic and non-polar solvents.[153] Polar protic solvents, such as water and alcohols, refer to a compound with a hydrogen atom attached to an electronegative atom like oxygen or nitrogen (O–H or N–H bond). Due to the electronegativity discrepancy between H and the heteroatoms, polar protic solvents are prone to donate protons. Polar aprotic solvents, like acetone, lack of O–H or N–H bonds, whereas contain a bond with a large bond dipole (like C=O, C=N or C≡N bond) leading to a net dipolar moment. In contrast, non-polar solvents contain bonds between atoms with similar electro negativities, such as carbon and hydrogen (*e.g.* hydrocarbon compounds). Choi and co-workers[154] compared the effect of solvent with different polarity, including ethanol (polar protic), acetone (polar aprotic) and ether (non-polar), on bio-oil quality during HDO process over Pt/C catalyst. Compared with non-polar ether solvent, ethanol and hydrogenated or reduced acetone could form hydrogen bonding with hydroxyl groups existing the bio-oil, resulting in effective bio-oil features improvement (including decreasing water content, lower viscosity and increasing heating value) by accelerating the further decomposition of organic compounds into light oil. As for lignin model compounds, the influence of solvent on the performance of guaiacol HDO process over Pt-based catalyst was investigated by Helliger and co-workers.[150c] Results showed that solvent could affect phase behaviour, solubility of reactant and H_2 as well as the catalyst's stability. Highest conversion and deoxygenation ability were seen when using non-polar solvents (*n*-hexane and *n*-hexadecane). It was speculated that polar solvents (oxygen-containing solvents) strongly adsorb on the active sites of the catalyst, which could block the adsorption and inhibit the deoxygenation of the reactants. The sintering effect of Pt nanoparticles after HDO process was also controlled by the different solvents with the following order: *n*-hexadecane ≈ *n*-hexane < diethyl ether < without solvent ≈ tetrahydrofuran ≈ carbon dioxide < 1-butanol < 1-octanol.

Water is well known for the promoting effect on the performance of HDO process of phenolic molecules. Vanillin HDO over Ni/NCB-900 catalyst was much better in terms of the conversion and selectivity towards partial deoxygenated product, 2-methoxy-4-methylphenol (MMP) using water as a solvent than using any other solvents like ethyl acetate, tetrahydrofuran (THF), dimethylformamide (DMF) and cyclohexane. It was speculated that doping with N atoms increased the hydrophilic properties of Ni/NCB, which could increase the dispersion of the catalyst in water and further improve the exposure of the catalyst to the reactant.[61] Furthermore, water seems to act as a co-catalyst favouring a direct deoxygenation pathway (DDO pathway, Figure 4, route 1) in HDO process of phenol over Ru/TiO_2 catalyst. DFT calculation and isotopic tracing results indicated that water adsorbed on hydroxylated or partially reduced TiO_2 could easily accept and donate protons across the Ru/TiO_2 interface and further lower the C–O cleavage barrier by donating a proton during the abstraction of the phenolic hydroxyl group, resulting the promoting effect for the production of benzene (Figure 15).[23c] The promoting effect of water

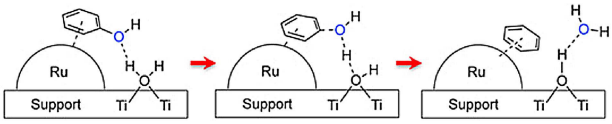

Figure 15. Main HDO reaction pathways of phenol over Ru/TiO_2 catalyst with assistant of water (reprinted from [23c] with permission of ACS. Copyright: 2015 ACS).

on DDO pathway could also be seen in *p*-cresol HDO process over Pt/C and Pt/Al_2O_3 catalyst. The formation of toluene was favoured with water as solvent since the low H_2 surface coverage and high polarity of water.[155] However, it was reported that the deoxygenation ratio of guaiacol over Rh/SAA-33 (SAA-33: Al/(Si + Al) = 0.33 mol mol^{-1}) in biphasic mixture (*n*-decane and water) was greater than that of solo water HDO process. The possible leaching of alumina from support can be observed when the water fraction (water fraction = water/(water + *n*-decane), mol mol^{-1}) was 1.0, which may lead to the rearrangement of the Rh/SAA-33 structure, leading to the deactivation of catalyst.[156]

Alcohols, like methanol and ethanol, are also typical solvents in HDO reactions due to their higher hydrogen solubility (7.8×10^{-7} mol cm^{-3} and 3.5×10^{-6} mol cm^{-3} for water and methanol, respectively, at 1 bar of H_2 and 25 °C[152]) and lower boiling point compared to water (64.7 °C and 78.4 °C for methanol and ethanol respectively), makes easier their separation from final products (*i.e.* smooth evaporation).[22] Hence, the performance of alcohols and water have been often compared in HDO. Zhou and co-workers[157] found that compared to methanol and ethanol, when water was employed as solvent, the HDO reaction could present a higher guaiacol conversion (96%) and high selectivity of cyclohexanol (70.9%) using a NiCo/Al_2O_3 catalyst at 200 °C and 5 MP of H_2. Daud and co-workers[22] detected the effect of methanol (methanol or water) on the HDO of simulated phenolic mixture (phenol: 50 wt.%, *o*-cresol: 25 wt.%, guaiacol: 25 wt.%) over NiFe/HBeta at 300 °C. Results showed that the addition of methanol to water can lower the selectivity towards oxygen-free products (53.59% and 10.77% for water and methanol, respectively). The distribution of products indicated that acetal reaction between methanol and intermediate, cyclohexanone, was occurred when methanol is selected as solvent. The negative effect of methanol-water mixtures compared with solo water in HDO process was favoured by kinetics study of individual steps of phenol. Results showed that the fast acetal reaction rate between ketone and

methanol (Figure 16, route 2) dominated the phenol conversion in methanol reaction system, resulting the low selectivity of the

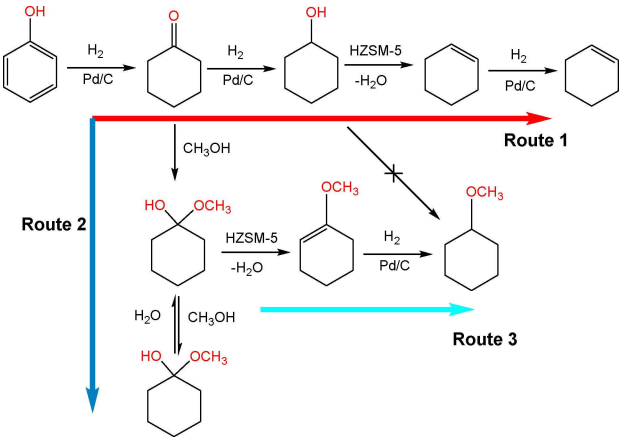

Figure 16. Reaction pathways for phenol hydrodeoxygenation over Pd/C and HZSM-5 catalyst in methanol (adopted from ref. [152]).

deoxygenated product, cyclohexane (Figure 16, route 1).[152] It could be concluded from these studies that alcohols are not proper solvents for catalytic HDO of phenolic compounds for the production of hydrocarbons. However, it has been reported that supercritical methanol[158] or ethanol[159] are efficient to improve the quality of bio-oil though catalytic upgrading process, although the complexity of supercritical media limits the mechanistic interpretation.

An overview of relevant works dealing with solvent effects in HDO reactions of model compounds is presented on Table 5. It is clear that the choice of the suitable solvent could greatly affect the reaction and therefore the successful catalysts' design targeting high activity and selectivity is unavoidably linked to the solvent selection.

2.3 Catalytic HDO using Hydrogen: Summary

The use of various mono- and bi-metallic catalysts as well as different solvents for HDO of phenolic compounds in the presence of H_2 have been carefully discussed in the preceding section. According to the reviewed literature, a strong effect of the active metallic phase is identified in the HDO process revealing different reaction pathways (which involve a marked effect on the conversion and selectivity) and tolerance to deactivation phenomena. Based on the numerous HDO investigations, Table 6a summarized the suitable metal-based catalysts which are promising for the production of particular deoxygenated compounds through phenolics HDO reactions. It seems clear that non-noble metal-based catalyst (like Mo, Co and Fe) are the sensible option for the production of aromatics due to their capacity to protect the benzene ring given their low hydrogenation ability. In contrast, Ni and noble metals (like Pt, Pd, Ru, Re) which favour the hydrogenation steps are suitable for the production of cyclohexanes. Bimetallic combinations, especially with oxyphilic metal, could improve HDO activity without the use of acid support (which favours coking resistance). The use of modifiers such as alkaline and alkaline-earth dopants is an interesting strategy to the stability of traditional hydrotreatment catalysts. As for the solvent choice, Table 6b shows a summary of the effect of solvent on the phenolics HDO process. Herein, polarity has a significant effect in the HDO process, in which water exhibits promoting effect in terms of conversion and selectivity in most cases. Alcohols are not recommendable when selecting solvent due to the inevitable parallel reaction (the acetal route) in HDO process. The application of biphasic solvent (mixture of polar solvent (water) and non-polar solvent) has the potential to enhance the degree of deoxygenation in phenolics or bio-oil HDO process and it could also facilitate products separation.

It is worth to mention that the crucial prerequisite for the implementation of biomass at a commercial level should be a low production cost which enable bio-resources to compete with crude oil derived fuels. There is no doubting that the supply of H_2 maintains the stumbling block for the industrial implementation of HDO from economic perspective. Moreover, efforts on increasing the economic performance of HDO technology lies on the application of non-noble metal catalysts, mild reaction condition (low temperature and hydrogen pressure) and high selectivity towards desired products. The fact that the catalytic activity of some well-formulated non-noble catalysts (i.e. Ni-based catalysts) have achieved comparable performance to that of expensive noble metal based catalysts in the HDO reaction is a promising step ahead. Attempts of HDO at atmospheric H_2 pressure (*using for example* Mo_2C and MoO_3 catalysts) have obtained desirable outputs for the production of aromatic compounds with minimized hydrogen consumption. Nevertheless, the design of highly active and stable catalysts remains as the key challenge which plays a significant role in the implementation of biomass in the future biorefinery schemes.

3. Hydrodeoxygenation Suppressing External H_2 Supply

Traditional HDO is a demonstrated technology with high efficiency for deoxygenation of bio-oils that can lead to bio-fuel and added value chemicals from biomass derivatives. Nevertheless, the "Achilles Heel" of this approach is the use of high pressure hydrogen-an expensive resource that impose a tremendous economic limitation to the implementation of HDO in large scale production units. In fact, this route is only viable when renewable hydrogen is available and cheap enough to be used in great quantities. In addition, bio-oil production mode is always multipoint spread due to the fact that biomass resources are widely dispersed and localised. Hence, the use of hydrogen as reactant (at high pressure) also imposes some extra concerns such as hydrogen transportation and storage and their respective safety implications. In this scenario, it will be ideal to develop a hydrogen free process to carry out the HDO reaction

Table 5. HDO of phenolic compounds using different solvent system.

Catalyst		Solvent	Reaction conditions	Model compounds	Major products	Sel. [%]	Conv. [%]	Reactor	Ref.	
Metal	Support		T [°C]	P [MPa]	t [h]					
Pt	SiO_2	none	180	5	5	guaiacol	methoxycyclohexanol	53	91	batch [150c]
							cyclohexanol	21		
							methoxycyclohexane	9		
							cyclohexane	3		
		n-hexane	180	5	5		methoxycyclohexanol	77	100	
							cyclohexanol	14		
							methoxycyclohexane	9		
							cyclohexane	2		
		n-hexadecane	180	5	5		methoxycyclohexanol	51	86	
							cyclohexanol	20		
							methoxycyclohexane	10		
							cyclohexane	8		
		1-butanol	180	5	5		methoxycyclohexanol	29	62	
							cyclohexanol	12		
							methoxycyclohexane	7		
							cyclohexane	16		
		diethyl ether	180	5	5		methoxycyclohexanol	82	46	
							cyclohexanol	8		
							methoxycyclohexane	3		
							cyclohexane	1		
		1-octanol	180	5	5		methoxycyclohexanol	51	12	
							cyclohexanol	3		
		carbon dioxide	180	5	5		methoxycyclohexanol	98	10	
							cyclohexanol	2		
		tetrahydrofuran	180	5	5		methoxycyclohexane	100	1	
Pt	H-MFI 90	none	180	5	5	guaiacol	methoxycyclohexanol	7	97	batch [150c]
							cyclohexanol	1		
							methoxycyclohexane	1		
							cyclohexane	35		
		n-hexane	180	5	5		cyclohexane	86	100	
		n-hexadecane	180	5	5		cyclohexane	93	100	
		1-butanol	180	5	5		methoxycyclohexanol	16	45	
							methoxycyclohexane	1		
							cyclohexane	49		
		diethyl ether	180	5	5		methoxycyclohexanol	9	86	
							cyclohexanol	4		
							cyclohexane	60		
		1-octanol	180	5	5		methoxycyclohexanol	24	15	
							cyclohexanol	50		
							methoxycyclohexane	1		
							cyclohexane	12		
		carbon dioxide	180	5	5		methoxycyclohexanol	6	43	
							cyclohexanol	1		
							cyclohexane	11		
		tetrahydrofuran	180	5	5		methoxycyclohexanol	49	5	
							cyclohexanol	6		
							methoxycyclohexane	5		
							cyclohexane	26		

Table 5. continued

Catalyst Metal	Support	Solvent	Reaction conditions T [°C]	Model compounds P [MPa]	Major products t [h]	Sel. [%]	Conv. [%]	Reactor	Ref.		
Ni	NCB-900	ethyl acetate	150	0.5	2	vanillin	4-hydroxymethyl-2-methoxyphenol (HMP)	≈73	≈7	batch	[61]
							2-methoxy-4-methylphenol (MMP)	≈27			
		water	150	0.5	2		HMP	≈35	≈74		
							MMP	≈65			
		THF	150	0.5	2		HMP	≈70	≈4		
							MMP	≈30			
		DMF	150	0.5	2		HMP	0	≈1		
							MMP	0			
		cyclohexane	150	0.5	2		HMP	≈67	≈17		
							MMP	≈35			
Ru	TiO_2	water	300	4.5	1	phenol	benzene	95	30	batch	[23c]
							cyclohexane	2.5			
		none	300	4.5	1		benzene	38	22		
							cyclohexane	40			
		octane	300	4.5	1		benzene	40	13		
							cyclohexane	24			
Rh	SAA-33	*n*-decane	250	4	1.4	guaiacol	none-Os	14	22[a]	batch	[156]
							1-Os	17			
		water + *n*-decane	250	4	1.4		none-Os	10	26[a]		
							1-Os	31			
		water	250	4	1.4		none-Os	4	15[a]		
							1-Os	21			
NiFe	Hbeta	water	300	0.6-1.1	4	phenol:*o*-cresol:guaiacol = 2:1:1	cyclohexanol	46.41	-	batch	[22]
							1-methyl-1,2-cyclohexanediol	21.66			
							1-methyl-1,2-cyclohexanediol, cis-	29.48			
							cyclohexane	2.45			
		water/methanol : 1:1 (v/v)	300	0.6-1.1	4	phenol:*o*-cresol:guaiacol = 2:1:1	cyclohexanol	68.80	-		
							1-methyl-1,2-cyclohexanediol	8.72			
							1-methyl-1,2-cyclohexanediol, cis-	18.15			
							cyclohexane	4.33			
		methanol	300	0.6-1.1	4	phenol:*o*-cresol:guaiacol = 2:1:1	cyclohexanol	89.23			
							1-methyl-1,2-cyclohexanediol	0	-		
							1-methyl-1,2-cyclohexanediol, cis-	5.71			
							cyclohexane	5.06			
NiCo	γ-Al_2O_3	water	200	5	8	guaiacol	cyclohexanol	70.9	96	batch	[157]
							1-methyl-1,2-cyclohexanediol	12.9			
							1-methyl-1,2-cyclohexanediol, cis-	8.1			
							cyclohexane	0.36			
		methanol	200	5	8		cyclohexanol	31.9	40.1		
							1-methyl-1,2-cyclohexanediol	29.4			
							1-methyl-1,2-cyclohexanediol, cis-	23.9			
							cyclohexane	2.2			
		ethanol	200	5	8		cyclohexanol	32.6	48.1		
							1-methyl-1,2-cyclohexanediol	32.8			
							1-methyl-1,2-cyclohexanediol, cis-	22.4			
							Cyclohexane	1.1			

[a] Degree of deoxygenation

Table 6. Hydrodeoxygenation of phenolic compounds over metal-based catalysts: effect of metal type and solvent.

6a. Effect of metal type

Model compounds	Deoxygenation mechanism	Metal-based catalyst	Deoxygenation product
phenol	hydrogenation→dehydration →hydrogenation	Ni, NiCo, CoP, ReO_x	cyclohexane
	dehydroxylation	MoO_3	Benzene
guaiacol	demethoxylation	ReS_2, CoMo	Phenol
	demethoxylation→ hydrogenation	NiCo, Ru	cyclohexanol
	demethoxylation→ dehydroxylation	Co, Pd-Fe	Aromatics
	demethoxylation→ hydrogenation→ dehydration→ hydrogenation	Ni_2P, Ni–Fe, Mo@Pt, Pt, Pd, Ru, ReO_x	cyclohexane
cresol	dehydroxylation	Mo_2C, MoO_3	Toluene
	hydrogenation→dehydration →hydrogenation	Ni_2P, Pd	methyl-cyclohexane
anisole	demethoxylation	Ni_2P, Co, Mo_2C, MoO_3, Ni@Pt	Benzene
	demethoxylation→hydrogenation	Ni_2P, Pt	cyclohexane
	hydrogenation	Ru	methoxy- cyclohexane
vanillin	hydrogenation reduction→ dehydroxylation	Ni, Pd	2-methoxy-4-methylphenol
	hydrogenolysis→ demethoxylation	Pd	*p*-cresol
syringol	demethoxylation→ hydrogenation→ dehydration→ hydrogenation	Ni	cyclohexane

6b. Effect of solvent

		Positive aspects	Negative aspects
Polar solvent	water	transferring protons (co-catalytic effect)	deactivation of catalyst
	alcohols	high solubility of H_2; low boiling point; separation	Inhibition reaction (acetal reaction); blocking the absorption of reactant and active sites of catalyst
Non-polar solvent	*n*-hexane, *n*-hexadecane, octane, *etc.*	prevent easy catalysts sintering	low solubility of phenolic compounds

with the same level of performance achievable by the conventional high pressure HDO processes in hydrogen atmosphere. This section of the review tackles this issue and aims to present the latest advances in this relatively unexplored and challenging area. Four strategies are worth exploring: (1) using a solvent as hydrogen donor (*i.e.* alcohols or formic acid). Hydrogen atoms will be provided through catalytic transfer hydrogenation (CTH) route; (2) Combined reforming-HDO where molecular hydrogen is produced via reforming (*i.e.* Aqueous phase reforming-APR) and consecutively be consumed in HDO process; (3) Combined metal hydrolysis-HDO where molecular hydrogen is produced via zinc hydrolysis process; (4) Non-thermal plasma (NTP) method. The collision of active electrons with oxygen-containing compounds could result in the cleavage of C–O, realising the purpose of deoxygenation. Obviously these four routes are relatively new technologies with less available literature to review but at the same time they offer great possibility for research and innovation.

3.1 Catalytic Transfer Hydrogenation/Hydrogenolysis (CTH)

The concept of catalytic transfer hydrogenation (CTH) was first proposed by Knoevenagel more than a century ago.[160] However, CTH technology has been shelved by the success of H_2-based HDO process in terms of pursuing high deoxygenation efficiency for the upgrading of bio-oils. The development of metal-based catalyst in recent years has aroused the attention for the application of CTH in bio-oil upgrading process. In recent years, CTH technology has been increasingly regarded as an alternative method for upgrading hemicellulose-based biomass. However, its application in HDO of lignin-derived feedstocks and phenolic compounds remain relatively unexplored. The hydrogenation of phenolic compounds can be effectively achieved by using a hydrogen donor solvent like formic acid,[161] 2-butanol,[162] and isopropanol.[163]

Catalytic transfer hydrogenation (CTH) is an effective strategy or adding H to the substrates without using H_2 molecular. Simple alcohols (like 2-propanol, methanol and ethanol) and other organic molecules (like hydrazine, tetralin, formic acid, cyclohexene, *etc.*) can donate hydrogen to the reaction media in hydrogenation and hydrodeoxygenation processes.[28,160,164] In this sense, the application of CTH using hydrogen donor solvents is an effective strategy to decrease the high cost of using H_2 as reactant in HDO processes. Conventionally, the CTH process occurs at less sever operation conditions. Metal-based catalysts are required to be effective for both hydrogenation and hydrogenolysis reaction with alcohols or formic acid as hydrogen donor.[28] It is effective for cleaving C–O bonds by hydrogenolysis reaction.[165] Hydrogen released from hydrogen donor solvent could react with hydrogen acceptors (reactant or intermediates) on catalytic active sites. An efficient catalyst for deoxygenation reaction by using hydrogen donor solvent are expected to have high potential for adsorption of both hydrogen donor and acceptor molecules. In fact, most of the successful catalysts discussed in Section 2.1 including mono-, bi- and multicomponent catalysts with hydrogenation and cracking capacity are suitable for this "*in-situ*"

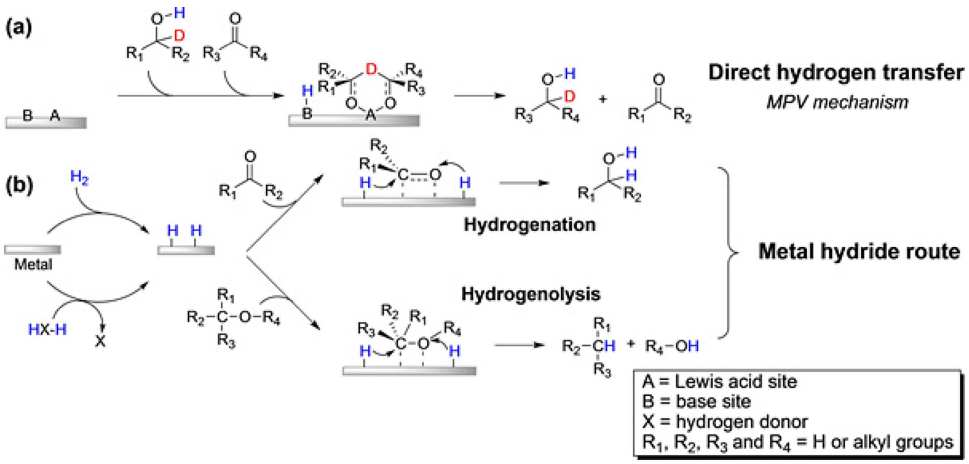

Figure 17. Common mechanisms for heterogeneous CTH reactions: (1) direct hydrogen transfer; (b) metal hydride route (reprinted from [28] with permission of ACS. Copyright: 2016 ACS)

HDO alternative and therefore we will not describe the catalytic systems with the same depth as previously on Section 3.1. New aspects such as reaction mechanisms become now relevant. In fact, two main mechanisms for heterogeneous CTH reactions existed: (a) Direct hydrogen transfer (Figure 17, route 1); (b) Metal hydride route (Figure 17, route 2).[28] Both hydrogenation and hydrogenolysis reactions could occur through metal hydride route. It is generally accepted that the mechanistic pathways of HDO process with molecular hydrogen or organic hydrogen donors converge after adsorbed atomic hydrogen is formed. However, the formation of negatively charged hydride species has been proposed as a surface intermediate with organic hydrogen donor,[165b,166] indicating some more substantial mechanistic differences may also exist in CTH process.

2-Propanol was employed as hydrogen donor for HDO guaiacol via CTH reaction. The conversion of guaiacol and 2-propanol in CTH process both follow the order of Ru/C > Pd/C > Ni/C, indicating Ru/C was superior catalyst for deoxygenation of guaiacol and dehydrogenation of 2-propanol. In guaiacol CTH process, 2-propanol could undergo dehydrogenation to produce H_2 along with an interesting by-product, acetone. The hydrogen produced from 2-propanol participated in the demethoxylation and subsequent hydrogenation of guaiacol to produce partial deoxygenated product cyclohexanol (>70% selectivity) over Ru/C catalyst. In the catalytic reaction system over bimetallic RuRe/C catalyst, cyclohexanol could be further converted into cyclohexane (selectivity: ≈60%) through C–O hydrogenolysis, showing a marked promotional effect of acid sites in Re (Figure 18).[167] Other investigation demonstrated that 2-propanol can also be used as hydrogen source for the transfer hydrogenolysis of aromatic alcohols. Raney Ni combined with β-zeolite catalyst in refluxing 2-propanol is an effective system for cleaving C–O bond resulting the deoxygenation of alcohols substituted at α-, β-, γ-, δ-, and ε-positions. In contrast, Raney Co-based catalytic effective system for α-substituted alcohols only. However, it showed greater selectivity by lack of ring reduction.[168] Recently, a new route was reported for the direct

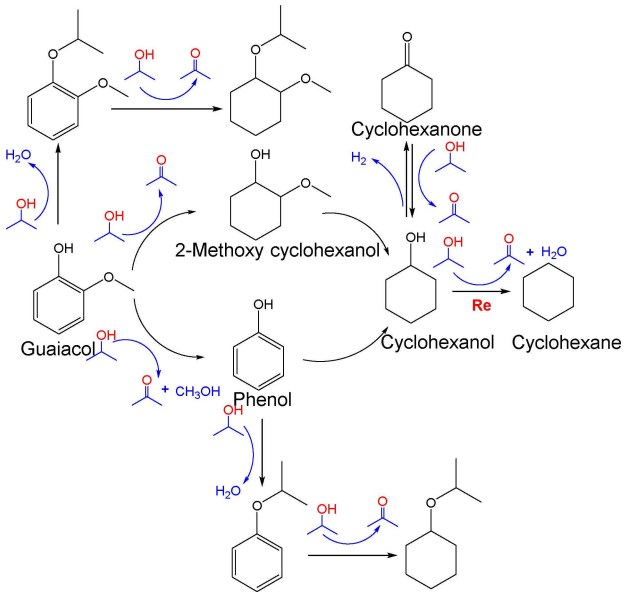

Figure 18. Reaction sequence of the CTH of guaiacol to cyclohexane over ReRu/C catalyst using 2-propanol as hydrogen donor solvent (adopted from ref. [167]).

deoxygenation of lignin model compounds, including *p*-cresol, 2-methoxy-4-methyl phenol, to aromatic compounds through CTH reaction over Ru/Nb_2O_5-SiO_2 catalyst with 2-PrOH (2-propanol) as the hydrogen source.[169] It is found that using 2-PrOH as hydrogen source was more selective to aromatic hydrocarbons than molecular hydrogen (yield: 84.0% vs 56.0%). The scheme of CTH reaction of *p*-cresol was proposed (Figure 19). Toluene is produced directly from DDO of p-cresol (Figure 19, route 1) when using 2-PrOH as hydrogen source. Meanwhile, only a small amount of products was generated through HYD pathway (Figure 19, route 2). High conversion of *p*-cresol (98.5%) and yield of toluene (84.0%) at 230 °C due to the great promotion effect of NbO_x species on the cleavage of C–O bond together with the proper transfer hydrogenation

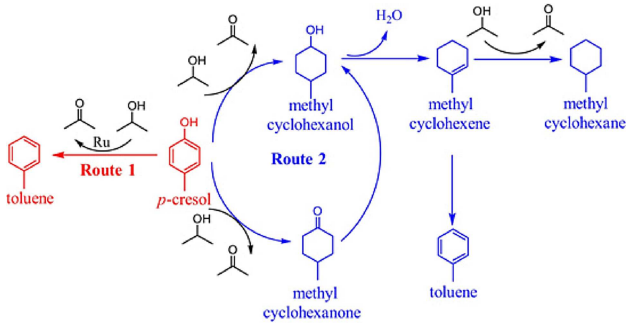

Figure 19. Reaction sequence on hydrodeoxygenation of *p*-cresol to toluene over Ru/Nb_2O_5-SiO_2 catalyst using water as solvents and 2-PrOH as hydrogen donor solvent (reprinted from [169] with permission of Elsevier. Copyright 2016 Elsevier).

activity of Ru nanoparticles. Rinaldi *et al.*[170] found that the selective HDO of phenol for producing benzene by using Raney Ni and H-BEA under mild conditions by using 2-PrOH as a hydrogen source. The main reactions are shown in Figure 20.

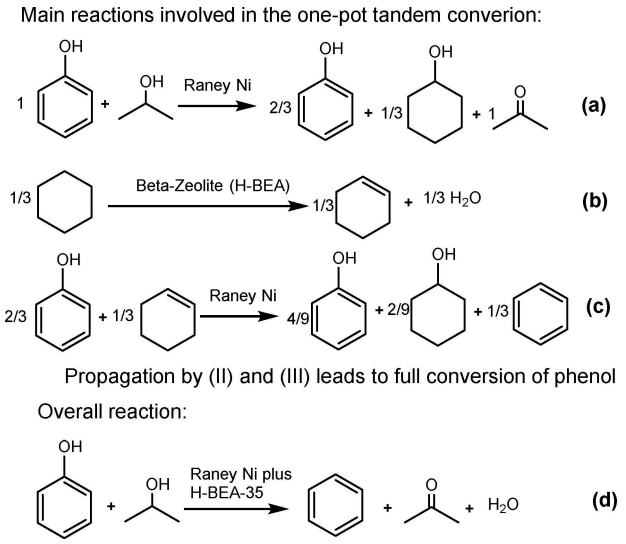

Figure 20. Simplified reaction pathway proposed of phenol to benzene over Raney Ni/H-BEA catalyst using 2-PrOH as hydrogen donor solvent (adopted from ref [170] with permission of Angewandte Chemie. Copyright: 2013 John Wiley and Sons).

Typically, under H_2 pressure, it is impossible for the combination of steps (a) and steps (c) in one-pot procedure to produce aromatic hydrocarbons. In contrast, based on the experimental investigation results, the one-pot procedure was realised by using 2-PrOH as a hydrogen donor. Reasons could be summarised that the lower hydrogenation ability of hydrogen donor solvent limited the hydrogenation of phenol (Figure 20, steps (a)).

Another type of popular hydrogen donor are small molecular acids, such as formic acid, acetic acid and oxalic acid. Acids are also one of the major components of bio-oil. For instance, acetic acid occupies up to 19% in bio-oil, depending on the nature of biomass and pyrolysis conditions.[171] These acids can undergo decomposition and reforming reactions to produce molecular hydrogen [Eqs. (2a), (3) and (4a)][172].However, formic acid and oxalic acid can also undergo the dissociation of C-OH to produce CO and H_2O [Eqs. (2b) and (4b)].[173] Water-gas shift (WGS) reaction between H_2O and CO could contribute to the production of H_2 since typical HDO temperature range (200-300 °C) is suitable for the WGS reaction [Eq. (5)][174]. In parallel, CO methanation could occur which decreases the hydrogen donation efficiency [Eq. (6)].

Decomposition and reforming of acid:

$$HCOOH \rightarrow CO_2 + H_2 \quad (2a)$$

$$HCOOH \rightarrow CO + H_2O \quad (2b)$$

$$CH_3COOH \rightarrow 2CO + 2H_2 \quad (3a)$$

$$CH_3COOH + H_2O \rightarrow 2CO_2 + 4H_2 \quad (3b)$$

$$COOHCOOH \rightarrow 2CO_2 + H_2 \quad (4a)$$

$$COOHCOOH \rightarrow CO_2 + CO + 2H_2O \quad (4b)$$

Water-gas shift reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (5)$$

Methanation:

$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad (6)$$

It was reported that the conversion and degree of deoxygenation (DOD) of phenol over Ru/MCM-41 with *in-situ* generated hydrogen from acid followed the order: formic acid oxalic acid > acetic acid. The superior performance of formic acid is related to the low conversion of acetic acid and high concentration of CO_2 derived from decomposition of oxalic acid.[172a] The better performance of formic acid compared to acetic acid could be also seen in RZ409 (Ni-based catalyst) catalytic system for *in-situ* hydrodeoxygenation of phenol.[172b] Formic acid is indeed well-known for its ability to donate hydrogen[175] and can be obtained from renewable carbohydrate materials through hydrothermal conversion process.[176] Formic acid is also well known as a by-product from the acidic hydrolysis of biomass.[177] Therefore, it usually be employed as hydrogen donor in lignin depolymerisation process,[175,178] which also shows the potential for its application in HDO process.

A more complex compound such as formic acid-triethylamine system is frequently used to enhance the dehydrogenation of formic acid.[179] Herein, N-doped carbon support could be a promising candidate for its utilization in CTH considering the similar chemical environment compared to nitrogen in triethylamine. It was reported that nitrogen-enriched mesoporous carbons (NMCs), which were synthesized through one-pot carbonization of biomass-derived glucose and harmless melamine with $ZnCl_2$, used in Pd-based catalytic system exhibited 2.9 times higher activity compared to nitrogen-free catalyst for converting vanillin to partially deoxygenated product, 2-

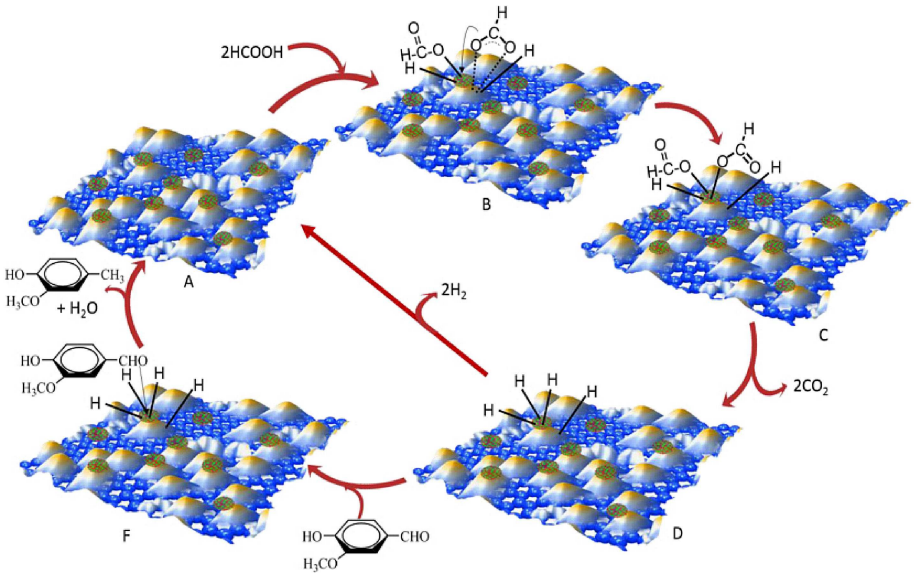

Figure 21. Proposed pathways for tandem hydrodeoxygenation of vanillin to 2-methoxy-4-methylphenol products over PdAg/Fe_3O_4/ N-rGO with formic acid as hydrogen donor solvent (reprinted from [180] with permission of ACS. Copyright: 2015 ACS).

methoxy-4-methylphenol (MMP). The HDO of vanillin with formic acid showed a different pathway compared with H_2 as hydrogen source. It is speculated that the hydrogenation of vanillin with formic acid is a tandem process consisting at least two steps: (1) Formic acid dehydrogenation on electron-deficient Pd ($Pd^{\delta+}$); (2) Vanillin hydrogenation on metallic Pd (Pd^0) without the formation of HMP. It should be pointed that the percentage of electron-deficient Pd ($Pd^{\delta+}$) phase is affected by the nitrogen species, and the strong Pd–N interaction generated the co-existence of $Pd^{\delta+}$ and metallic Pd (Pd^0), which resulted in Pd/NMC as an effective bifunctional nanocatalyst for formic acid dehydrogenation together with the subsequent vanillin hydrogenation.[177] Also dealing with vanillin, Singh and co-workers[180] developed a series of multicomponent Pd–Ag catalysts supported on Fe_3O_4/nitrogen-doped reduced graphene oxide (N-rGO) for their application in HDO of vanillin using formic acid as hydrogen source. These catalysts are very effective in dehydrogenation formic acid to form molecular hydrogen. The *in-situ* generated H_2 subsequently participated for de-carbonyl group reaction. More interestingly, the benzene rings were well protected in formic hydrogen donor solvent system, with significant selectivity (99%) of 2-methoxy-4-methylphenol products (Figure 21). HDO process over Pd-based catalyst by *in-situ* generated hydrogen from formic acid was investigated by Zeng and co-workers.[181] The catalytic activity for deoxygenation of phenol followed the order of $Pd/SiO_2 >$ $Pd/MCM41 > Pd/CA > Pd/Al_2O_3 > Pd/HY \approx Pd/ZrO_2 \approx Pd/CW >$ $Pd/HSAPO\text{-}34 > Pd/HZSM\text{-}5$. The superior performance of Pd/SiO_2 resulted from its proper pore structure, large specific surface area and the high level of Brønsted acid sites in SiO_2 support. However, formic acid is not suitable for the deoxygenation of phenol over Pd/AC catalyst, since hydrogenation happened without any deoxygenation process.[161] Similar results showing poor performance of formic acid in HDO of phenol was also observed in Ni-based catalytic system. CO_2 generated from decomposition of formic acid was found to hamper the HDO of phenol, due to the competitive adsorption of phenol with CO_2 on the Al_2O_3 support.[182] Furthermore, Xiong and co-workers[183] conduct the HDO process of bio-oil in formic acid-methanol solvent system over Raney Ni and zeolites-supported Pd and Ru catalysts. H_2 and CO_2 produced from decomposition of formic acid have their own mission. H_2 acted as reductant the HDO of bio-oil while CO_2 could dissolve in methanol to form a CO_2-CH_3OH expanded liquid. Results indicated that Raney Ni and zeolites-supported Ru were effective for improving property of bio-oil. Specifically, deoxygenation ratio of bio-oil through *in-situ* HDO process reached 8.9 wt.% and 9.7 wt.% at 270 °C, respectively, when Raney Ni and zeolites-supported Ru were employed in HDO process.

Hydrocarbon compounds, such as decalin and tetralin, can also be used as hydrogen donor in bio-oil upgrading processes or simultaneous liquefaction and HDO of biomass.[184] Typically, decalin and tetralin could adsorb on catalytic active sites and undergo dehydrogenation process to produce naphthalene.[185] Hydrogen atoms provided by decalin and tetralin could be released to participate in the hydrogenation reaction via CTH mechanism.[186] The CTH of phenolic compounds, including phenol, *o*-cresol and guaiacol was investigated by employing decalin and tetralin as hydrogen donor solvent over carbon supported Pd and Pt catalysts.[187] Pt/C performs better than Pd/C when tetralin was used as hydrogen donor in the CTH process. Very importantly, conversions of phenol, *o*-cresol and guaiacol over Pt/C using decalin as hydrogen source were almost as high as those achieved by a conventional HDO process. Inferior performance was observed when tetralin was used as hydrogen source in terms of phenolics conversion. Results could be attributed to the stronger adsorption ability of tetralin on catalytic active sites due to the present of benzene

ring in its chemical structure. The blocking effect tetralin leaded to decreased ratio of reactant absorbed on the active sites of catalyst, resulting the lower HDO activity in CTH process.[187] The main investigation results of hydrodeoxygenation by using hydrogen donor solvent of phenolic compounds are listed in Table 7. It should be pointed that the separation of dehydrogenized by-products (*i.e.* formaldehyde, naphthalene) needs further energy input. In addition, the catalysts' deactivation is a key factor to consider given the complex reaction mechanism existing in HDO with hydrogen donor participation. For example, the CO, produced from the dehydration of formic acid or generated as by-product from Sabatier reaction of CO_2, is frequently a poison for active centres of catalysts.[188] More importantly, catalyst's recycling and long term stability, especially given the acidic reaction environment (*i.e. in-situ* HDO with formic acid) are mandatories requisites to be considered for practical applications of CTH.

3.2 Combined Reforming and *in-situ* HDO Process

Methane and alcohols can be regarded as attractive alternatives to replace external H_2 supply since it can act as hydrogen donor by releasing H_2 via reforming reactions.[189] The produced hydrogen can be directly utilised for the hydrodeoxygenation of phenolics or bio-oils. This idea resembles part of the discussion in the previous section and in fact organic acids such as formic acid and acetic acid as well as alcohols such as propanol can be reformed to donate hydrogen. However, since reforming is a well-known process on chemical industry, in this section we intend to be more specific and focus on two particular processes: steam reforming (SR) and aqueous phase reforming (APR).

The strategy of combining methane reforming and deoxygenation of biomass derived oxygenates was proposed by Fernando and co-workers.[29b] They presented that reforming of methane or any short chained hydrocarbon could be catalytically coupled with biomass derived oxygenates to dehydrate and produce deoxygenated hydrocarbons over a zeolite-based catalyst. The hydrogen gas formed "*in-situ*" during methane steam reforming serves as a reactant for oxygenated pyrolytic vapour aromatization. Conversely, the water formed during oxygenate aromatization serves as a reactant for methane steam reforming. This process uses short chained hydrocarbons (such as methane or natural gas) to instigate HDO suppressing the need of using expensive molecular hydrogen. The simplified reactions sequence for integrating methane reforming and oxygenates deoxygenation process is presented below [Eq. (7)–(9)]:

Methane steam reforming:

$$CH_4 + H_2O \rightarrow H_2 + CO_2 \quad (7)$$

Biomass oxygenates dehydration and aromatization:

$$C_xH_yO_z + H_2 \rightarrow BTEX + H_2O \quad (8)$$

Overall reaction:

$$C_xH_yO_z + CH_4 \rightarrow BTEX + CO_2 \quad (9)$$

where BTEX is benzene, toluene, ethylbenzene and xylene.

Specifically, in view of the high activity of Pt-based catalysts in both reforming and hydrogenolysis process,[190] Varma *et al.*[191] use methane as reductant in the deoxygenation of guaiacol over Pt-based catalysts. Results indicated that by using Pt/C catalyst, and CH_4 as H_2 source fairly good deoxygenation performance in term of O/C was obtained (from 0.28 decreased to 0.22, at 300 °C and 1 atm). However, the lifetime of Pt/C catalyst was short (< 3 h). Using a bimetallic formulation, in particular Pt–Bi/C the lifetime of the catalyst was prolonged (no significant deactivation was observed in upon addition of small quantities of Bi as promoter. The gas products distribution is also altered by the use of CH_4 as H_2 donor compared that obtained when H_2 is directly supply to the reaction. For both catalysts Pt/C or PtBi/C, CO and CH_4 were generated when H_2 is directly used, whereas, CO and C_2H_6 was produced from the CH_4 reforming strategy. Based on the product distribution and their prior work, Varma's team proposed a conceptual reaction process.[192]

For deoxygenation in molecular hydrogen condition:

$$R_2O + 2H_2 \rightarrow 2RH + H_2O \quad (10)$$

For deoxygenation in methane condition:

$$R_2O + 4CH_4 \rightarrow 2RH + 2\,C_2H_6 + H_2O \quad (11)$$

It was proposed that CH_4 decomposed on Pt surface and further contributed one H atom for guaiacol deoxygenation, which was similar to that of H_2-based HDO process, whereas the residual methyl combines with another methyl resulted in the formation of ethane. They further set kinetic models for deoxygenation of guaiacol using methane as hydrogen source successfully obtaining a good matching between the model predicted values and the experimental data.[193] Biomass-derived oxygenated hydrocarbon could also be used as alternative of external H_2 considering its ability of producing H_2 through aqueous-phase reforming (APR) process. Fisk and co-workers[29a] investigated *in-situ* HDO of bio-oil over a series of Pt-based catalysts (including Pt/CeO_2, $Pt/CeZrO_2$. Pt/TiO_2, Pt/ZeO_2, Pt/ASA and Pt/Al_2O_3), in which Pt/Al_2O_3 catalyst exhibited the highest activity in terms of the degree of deoxygenation of bio-oils. The integrated APR and HDO process of bio-oils was presented as follow (Figure 22). Light oxygenates mainly undergo reforming route to produce CO_2 and H_2, with C–O bond breaking as a minor pathway. In a parallel process, aromatic compounds could undergo C–O cleavage or hydrogenation to produce benzenes and cyclohexanes.

Following this strategy, Wang et al.[194] investigated the *in-situ* HDO of bio-derived phenols in methanol-water solvent over Raney Ni and Nafion/SiO_2 catalyst. In this process hydrogen

Table 7. CTH of phenolic compounds using hydrogen donor solvent.

Catalyst Metal	Support	Hydrogen donor solvent	Reaction conditions T [°C]	P [MP]	t [h]	Model compounds	Major products	Sel. [%]	Conv. [%]	Reactor	Ref.
							cyclohexane	0.8			
Ru	C	2-propanol	300	2 (N_2)	5	guaiacol	cyclohexanol	70.2	99.3	batch	[167]
							2-methoxy cyclohexanol	11.4			
							ethers	4.0			
							cyclohexane	38.3			
RuRe	C	2-propanol	300	2 (N_2)	5	guaiacol	cyclohexanol	44.7	99.1	batch	[167]
							2-methoxy cyclohexanol	2.2			
							ethers	4.3			
							cyclohexane	57.0			
RuRe	C	2-propanol	340	2 (N_2)	5	guaiacol	cyclohexanol	24.1	99.0	batch	[167]
							2-methoxy cyclohexanol	1.1			
							ethers	6.0			
							toluene	85.27			
Ru	Nb_2O_5-SiO_2	2-PrOH + water	230	0.6	20	*p*-cresol	methyl cyclohexane	4.57	98.5	batch	[169]
							methyl cyclohexene	0.51			
							toluene	80.92			
Ru	Nb_2O_5-SiO_2	H_2	230	0.6	3	*p*-cresol	methyl cyclohexane	12.43	69.2	batch	[169]
							methyl cyclohexene	0.72			
Raney Ni	β-zeolite (H-BEA-35)	2-propanol	160	-	4	phenol	benzene	82	100	heating block	[170]
Pd	NMC	formic acid	150	0.5	3	vanillin	2-methoxy-4-methylphenol	100	> 99	batch	[177]
							2-methoxy-4-methylphenol	69			
Pd@Ag	C	formic acid	130	0.1	6	vanillin	2-methoxyphenol	17	100	batch	[180]
PdAg	N-rGO	formic acid	130	0.1	6	vanillin	2-methoxy-4-methylphenol	98	100	batch	[180]
PdAg	Fe_3O_4/N-rGO	formic acid	130	0.1	6	vanillin	2-methoxy-4-methylphenol	99	100	batch	[180]
							cyclohexane	43.7			
Ru	MCM-41	formic acid	280	1	4	phenol	cyclohexene	2.1	73.9	batch	[172a]
							benzene	14.2			
							cyclohexane	≈ 75			
Pd	SiO_2	formic acid	280	1	4	phenol	cyclohexanone	≈ 8	≈ 90	batch	[181]
							benzene	≈ 8			
							cyclohexanone	≈ 17.6			
Pd	C	formic acid	300	2-12	3	phenol	cyclohexanol	≈ 9.4	14	batch	[172b]
							cyclohexanone	≈ 15.4			
Ni (RZ409)		formic acid	300	2-12	3	phenol	cyclohexanol	≈ 9.7	42.2	batch	[172b]
							cyclohexane	≈ 7.3			
							methylcyclohexanone	65.92			
Pt	C	H_2 (gas) water	275	1.6	4	*o*-cresol	methylcyclohexanol	10.91	97.30	batch	[187]
							toluene	23.17			
							methylcyclohexanone	28.02			
Pt	C	decalin	275	0.1	4	*o*-cresol	methylcyclohexanol	50.04	88.50	batch	[187]
							toluene	21.94			
							phenol	44.43			
Pt	C	H_2 (gas) + water	275	1.6	4	guaiacol	cyclohexanone	25.31	100	batch	[187]
							cyclohexanol	25.51			
							phenol	7.86			
Pt	C	decalin	275	0.1	4	guaiacol	cyclohexanone	19.57	95.15	batch	[187]
							cyclohexanol	63.73			

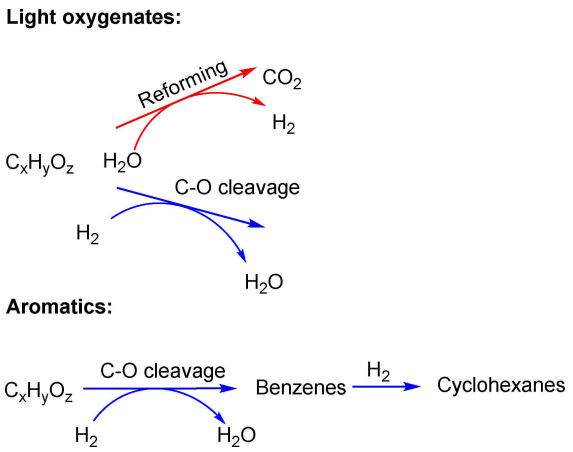

Figure 22. Simplified reaction scheme for model bio-oil upgrading over Pt/Al_2O_3 catalyst via combined reforming-HDO route (adopted from ref. [29a])

produced from APR of methanol (Eq. 12) could replace external molecular hydrogen in HDO process thus making the overall process more economically attractive. Reaction pathways of the process are shown in Figure 23. In this process, water derived from cyclohexanol through dehydration can served as reactant for methanol APR to produce hydrogen. Hence the high water content in bio-oil was avoided compared to traditional strategies.

APR of methanol:

$$CH_3OH + H_2O \rightarrow 3H_2 + CO_2 \quad (12)$$

Feng et al.[195] investigated the *in-situ* HDO of biomass-derived phenolic compounds (*i.e.* catechol, 4-methyl-guaiacol and 6-methoxy-guaiacol) in methanol-water solvent system over Raney Ni/HZSM-5 or H-Beta catalyst. Results showed that phenolic monomers could be efficiently converted into hydrocarbons (conversion: $>97\%$; selectivity of cyclohexane: $\approx 90\%$) over Raney Ni/HZSM-5 catalyst at 220 °C and 0.5 MPa.[195a] The reaction mechanism of integrated methanol reforming and *in-situ* hydrodeoxygenation of phenolics was proposed as follow (Figure 24). Phenolic compounds are initially hydrogenated to 2-methoxyl-cyclohexanol, followed by being dehydrated and hydrolysed to form methanol cyclohexanes. This *in-situ* HDO process over bifunctional catalysts provided an effective route for the upgrading of bio-oil or phenolic compounds into added value hydrocarbon products.

Polyols such as glycerol, ethylene glycol, xylitol and sorbitol, which can be derived from thermal conversion of lignocellulose can also be used as hydrogen source for the HDO process.[196] Glycerol is widely studied one of by-products from the manufacture of biodiesel. Glycerol is a promising hydrogen source for HDO process considering its low price and high availability.[197] Even though HDO of phenolic-type lignin model compounds is the main focus of this review, the investigation of de-hydroxylation of other compounds, such as glycerol, could provide guidance for that of phenolics in terms of the selection of catalysts and clarifying de-hydroxylation mechanism. For instance, Lemonidou can co-workers did a series investigation of glycerol HDO with *in-situ* H_2 formation through APR reaction (*i.e.* methanol and ethanol).[198] Identification of the hydrogen source is of interest for clarifying the reaction mechanism in the process. Apart from the methanol APR reaction [Eq. (12)], the H_2 could formed through another two reactions [Eqs. (13) and (14)].[199]

Glycerol APR:

$$C_3H_8O_3 + 2H_2O \leftrightarrow 7H_2 + 3CO_2 \quad (13)$$

Water-gas shift:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (14)$$

Isotopic tracing results showed that methanol reforming was the main hydrogen source (70% of total H_2) in this tandem process in a Cu bulk ($CuO–ZnO–Al_2O_3$) catalytic system.[198a] The optimisation of reaction conditions in a further study showed that glycerol was almost fully converted (95.9%), with high

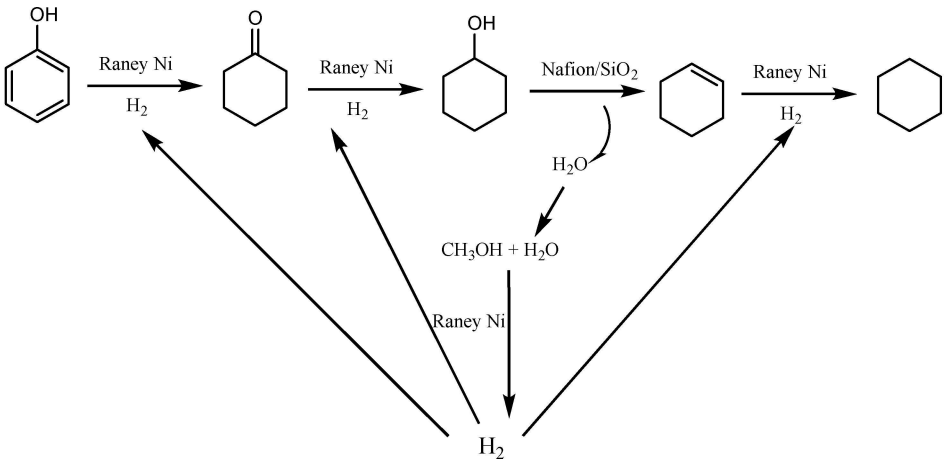

Figure 23. Reaction pathways of *in-situ* hydrodeoxygenation of phenol over Ni-based catalyst by using methanol as hydrogen source (reprinted from [194] with permission of Elsevier. Copyright: 2015 Elsevier).

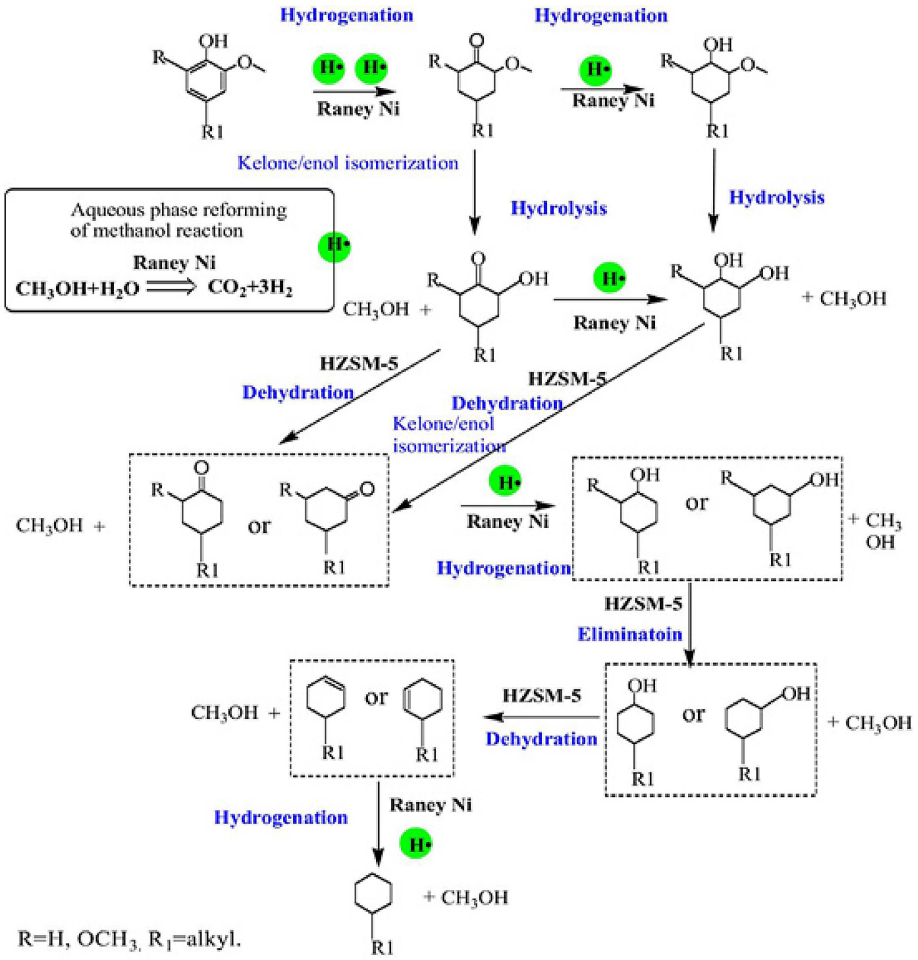

Figure 24. Proposed *in-situ* hydrodeoxygenation mechanism of lignin-derived phenolic monomers by using methanol APR as hydrogen source (reprinted from [195a] with permission of Elsevier. Copyright: 2017 Elsevier).

selectivity (79.4%) of 1,2-propanediol at 250 °C with methanol and glycerol ratio of 4:1 *v/v* over the Cu catalyst. It was proposed that metallic Cu^0 efficiently catalyses glycerol hydrodeoxygenation, while methanol reforming is mainly catalysed by metallic Cu^0 and facilitated by the interaction of Cu^0 with $ZnO\text{-}Al_2O_3$ structures.[198b] Representative results of combined reforming and HDO of phenolics are listed in Table 8.

3.3 Hydrogen Production from Metal Hydrolysis Reaction Followed by *in-situ* HDO Process

Water splitting over a metallic surface is an interesting approach to obtain cheap and sustainable hydrogen. Active metals, like beryllium (Be), aluminium (Al), zinc (Zn), magnesium (Mg), calcium (Ca), lithium (Li), sodium (Na), and potassium (K) can react with water to produce H_2. This strategy also own some advantages: (1) energy can be released in this process; (2) some products from metal hydrolysis, such as ZnO, MgO and AlOOH have catalytic properties.[200] The hydrolysis of metal (mainly, Al and Zn) was investigated as hydrogen source in deoxy-liquefaction of biomass[201] and coal,[202] exhibiting potential for its utilization via *in-situ* HDO process. The main channel for the production of H_2 from Zn or Al hydrolysis represent as follow [Eqs. (15) and (16)].[203]

$$Zn + H_2O = ZnO + H_2 \quad (15)$$

$$Al + 2H_2O \rightarrow AlOOH + 1.5H_2 \quad (16)$$

Recently, Cheng and co-workers[30] applied this concept to engineer a tandem process where hydrogen produced *in-situ* by using Zn/ZnO thermochemical cycle approach is utilised for bio-oil upgrading via hydrodeoxygenation process over a Pd/C catalyst[204] the bio-oil upgrading to realise the *in-situ* hydrogen generation. The oxygen content of upgraded bio-oil decreased by 10%~18% compared to the original bio-oil. This investigation provides an original orientation for the upgrading bio-oil by using cheap water as hydrogen donor. They further proposed a scheme of the looped-Zn catalysis for catalyst recycle and bio-oil HDO (Figure 25).[205] It is showed that the Zn regeneration could be realized through a high temperature solar electrothermal reactor and a subsequent condenser system.[206] The recovered Zn will be reused for *in-situ* hydro-

Table 8. Tandem reaction of reforming and consequent HDO of phenolics.

Catalyst Metal	Support	Reforming reactant	Reaction conditions T [°C]	P [MPa]	t [h]	Model compounds	Major products	Sel. [%]	Conv. [%]	Reactor	Ref.
Pt	C	CH_4:N_2 = 1:1	300	1	1	guaiacol	cyclopentanone	23.1	≈82	fixed-bed	[191]
							catechol	13			
							phenol	35.4			
Pt-Bi	C	CH_4:N_2 = 1:1	300	1	1	guaiacol	cyclopentanone	24.9	≈83	fixed-bed	[191]
							catechol	11.5			
							phenol	34.5			
Pt-Bi	C	CH_4:N_2 = 1:1	450	1	5	guaiacol	-	-	≈97	fixed-bed	[191]
Raney Ni	Nafion/SiO_2	CH_3OH-water	200	0.9	6	phenol	cyclohexane	55.8	100	batch	[194]
							cyclohexane	31.2			
Ni	HZSM-5 (Si/Al = 25)	CH_3OH-water	220	0.5	7	guaiacol	cyclohexane	93.4	100	batch	[195a]
Ni	H-Beta (Si/Al = 25)	CH_3OH-water	220	0.5	7	guaiacol	cyclohexane	85.6	100	batch	[195a]

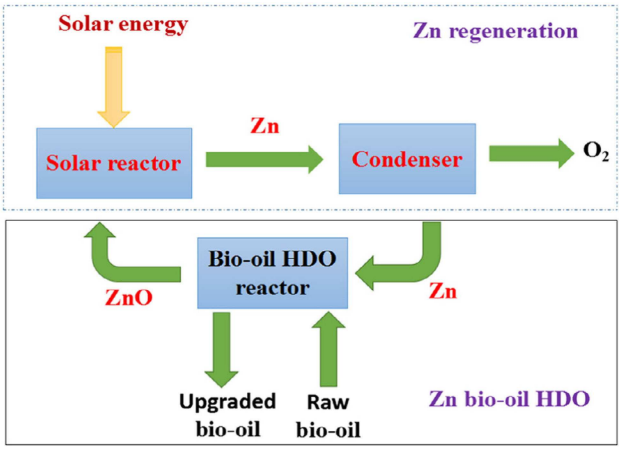

Figure 25. Proposed scheme of looped-Zn catalysis for catalyst recycle and bio-oil HDO process (adopted from ref. [205]).

deoxygenation of bio-oil for long-term process. In this way, the hydrogen generation from Zn hydrolysis could be recovered. The cost of HDO process might be reduced since the hydrogen was derived from water and the recycle of Zn was powered by free solar energy. The economic advantage of this strategy impels specific explorations about hydrodeoxygenation of phenolics, which could maximize the deoxygenation ratio in the HDO process and clarify the specific mechanism of this tandem reaction.

3.4 Non-Thermal Plasma (NTP) Technology

A completely different and novel approach is the utilization of non-thermal plasma (NTP), for deoxygenation of bio-oils without using a hydrogen source.[80] Plasma, produced from containing highly energetic species (*i.e.* ions, electrons).[207] The effective collision (inelastic collisions) of active electrons the ionization of neutral gases, is partially ionized gas with the molecules of bio-oil compounds could result in the cleavage of weaker bonds, such as C–O or C–H, resulting on the removal of oxygen atoms.[208] Numerous parameters could affect the efficiency of deoxygenation performance including pulse repetition frequency (PRF), carrier gas flow rate, gas distance, remediation time, pin number and plate electrode diameter (PED) *etc.* An interesting advantage of the non-thermal plasma process is that it requires mild operation conditions. Indeed, the reaction is typically conducted at atmospheric pressure and ambient temperature. Such mild reaction conditions not only eliminate the necessity high pressure of hydrogen supply in conventional HDO process but also minimizes the catalysts' deactivation which is a frequent bottleneck in HDO commercial implementation.

Rahimpour and co-workers did a series of experiments for upgrading of anisole and 4-methyanisole by employing a dielectric barrier discharge (DBD) plasma or corona plasma reactor (Figure 26).[80,208–209] For the upgrading of anisole over Al_2O_3 supported catalyst in DBD plasma reactor the activities of

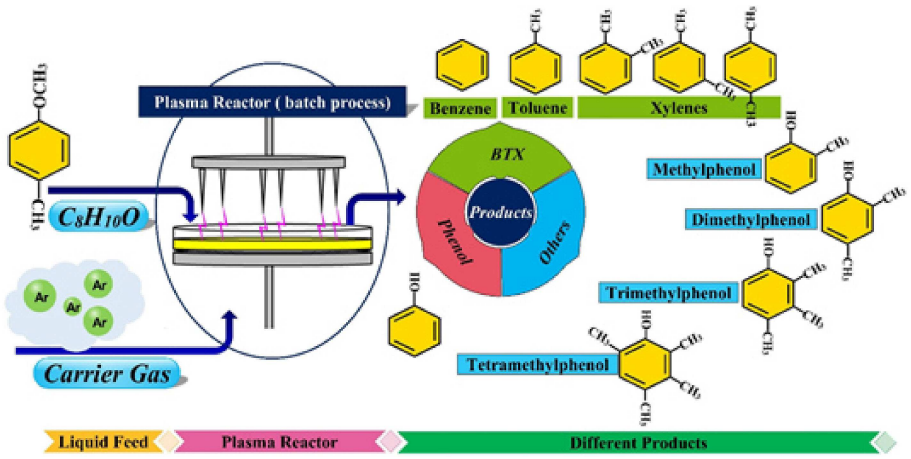

Figure 26. Scheme of Non-Thermal-Plasma (NTP) for upgrading phenolic compounds (anisole) (reprinted from [80] with permission of Elsevier. Copyright: 2017 Elsevier).

the catalysts in terms of the conversion ratio could be followed the order: $NiMo/Al_2O_3 > Pt/Al_2O_3 > CoMo/Al_2O_3 > PtRe/Al_2O_3 > Al_2O_3 >$ plasma alone. However, the deoxygenation ratio was low since the primary product is oxygen-contained compounds, 4-methylanisole (selectivity ≈ 73%).[209a]

In contrast, Pt–Re/Al_2O_3 catalyst is effective for oxygen removal from 4-methylanisole, with 47% deoxygenation degree in catalytic pulsed DBD plasma reactor system.[208] In a corona plasma reactor, the corona discharge is able to decompose methyl radical and produce hydrogen radical for the deoxygenation of reactant. The predominant upgraded compounds, phenol and BTX were produced through demethylation, transalkylation, hydrogenolysis, demethoxylation and methane decomposition reactions happened in the corona plasma reaction system. Reaction mechanism changed with the energy and collisions in the discharge zone, with increase energy and number of collisions, the reaction mechanism changed from mechanism A to C as shown in Figure 27.[80]

Although still in an early stage, plasma catalysis may become a realistic approach to conduct HDO without the need of external hydrogen supply. The ability to run at very mild conditions in terms of temperature and pressure along the absence of expensive hydrogen as reactant are enormous advantages of this technology. In contrast, the amount of energy to run the plasma reactor could represent a handicap. In the literature there is a clear need to develop accurate energy balances are needed to ascertain the future of plasma catalysis as a realistic alternative for bio-oil upgrading. In any case, the latest contributions on this field look promising and are opening new avenues for multidisciplinary research. On Table 9 we have summarized represented results of the recent publications in this area.

3.5 Catalytic HDO Suppressing External H_2 Supply: Summary

Avoiding external hydrogen supply is a crucial factor for the implementation of the HDO processes at commercial level. A variety of alternatives are available with a different degree of maturity. In this review we have covered four innovative strategies including catalytic transfer hydrogenation/hydrogenolysis (CTH), combined reforming& hydrodeoxygenation, metal

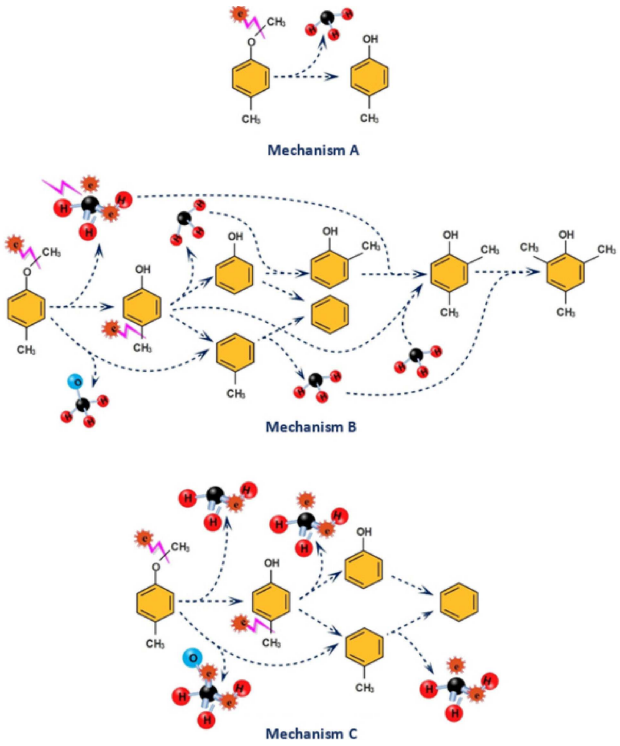

Figure 27. Reaction mechanisms of the combination of methyl group decomposition and hydrodeoxygenation of 4-methylanisole (reprinted from [80] with permission of Elsevier. Copyright: 2017 Elsevier).

Table 9. Plasma upgrading of phenolic compounds by using non-thermal plasma (NTP) method.

Reactor	Catalyst	Model compounds	Major products	Sel. [%]	Conv. [%]	Ref.
Dielectric Barrier Discharge (DBD) plasma reactor	Mo–Ni/Al_2O_3	anisole	4-methylanisole phenol 2-methyphenol 4-methyphenol benzene	≈73 ≈17 ≈4 ≈1 ≈1	81	[209a]
DBD plasma reactor	Pt–Cl/Al_2O_3	4-methylanisole	dimethylphenol 4-methylphenol p-xylene phenol	≈23 ≈21 ≈17 ≈6	98.7	[208]
DBD plasma reactor	Pt–Re/Al_2O_3	4-methylanisole	dimethylphenol 4-methylphenol p-xylene phenol	≈15 ≈17 ≈21 ≈8	≈60	[208]
Corona plasma reactor	none	4-methylanisole	phenol BTX methylphenol	≈47 ≈15 ≈24	≈78	[80]

hydrolysis with subsequent hydrodeoxygenation and non-thermal plasma (NTP) technology. All of these processes could represent solution to replace the utilization of external molecular hydrogen for hydrodeoxygenation of phenolics or bio-oils. CTH and combined reforming-HDO require advanced catalysts able to overcome multiple steps. The advantage for these two processes is that they can adapt lessons from traditional HDO (with external hydrogen input) to achieve the optimum catalysts design. In general, CTH by using hydrogen donor solvent is favourable for effective partial deoxygenation of phenolics. In contrast, reforming (of methane or methanol) followed by *in-situ* hydrodeoxygenation is a very competitive route due to its high efficiency for total deoxygenation showing enormous potential for practical application. Metal hydrolysis (or water splitting over a Zn surface) with consequent HDO is an attractive approach given that water (a cheap and available resource) is used as hydrogen source. However, the regeneration of metal needs high energy input. Financial investment for setting up the solar electrothermal reactor-condenser reaction systems at industrial scale needs to be considered. More importantly, the solar energy powered metal-regeneration process cannot realize the continuous production of metal. Non-thermal plasma (NTP) technology is overshadowed compared to the other three strategies due to the low selectivity of deoxygenated products, although it owns the advantage of fairly mild reaction conditions. Recently, efforts on HDO using plasma are focused on enhancing the HDO performance in a non-catalytic scenario. This strategy economizes the capital and operational costs associated to catalyst production, recovery, deactivation and regeneration. The HDO by plasma technology will certainly help to develop further this route which can be a realistic alternative for economical viable HDO processes in the near future.

4. Conclusions and Perspectives

The design of advanced catalysts maintains its crucial status in the application of hydrodeoxygenation processes for bio-resources upgrading. Although HDO technology has been developed for decades, the supply of external H_2 has been an obstacle which limits the implementation of HDO at a commercial level ever since. Novel strategies including transfer hydrogenation/hydrogenolysis (CTH), combined reforming & hydrodeoxygenation, metal hydrolysis with subsequent hydrodeoxygenation and non-thermal plasma (NTP) have been developed as alternative methods which can avoid the supply of external H_2. Small organic molecules (such as alcohols, acids, polyols) which are by-products derived through thermal conversion of biomass are promising hydrogen sources for *in-situ* HDO process considering their low price and high availability. Within the alternative methods for hydrogen-free HDO, combined *in-situ* reforming and hydrodeoxygenation is the most developed so far and seems to be a reliable option. Plasma catalysis is an emerging approach which shows promising results for an economically viable oxygen removal process suppressing external hydrogen input but still the complexity of the process requires further research to validate this route. CTH and metal hydrolysis have also shown potential applicability for oxygen removal on model compounds leading to added value products. Overall, all the reviewed alternatives outstand as viable options to overcome the safety concerns and high cost associated to the traditional HDO for bio-resources valorisation. However, investigations are still insufficient, especially for the design of multitask catalysts able to carry out several simultaneous steps (*i.e.* reforming or dehydrogenation, and hydrodeoxygenation). In addition, a major question arises on whether these routes are still valid when raw biomass feedstocks are considered. Some studies on the open literature already shown that complex feedstock can be treated using some of the discussed approaches. In any case the information gathered with model compounds is pivotal to design the upgrading process of real feedstocks.

The future foresees high activity in this multidisciplinary area at the interface of chemistry/chemical engineering with innovative ideas arising. For example, a future challenge could be the use of water as a hydrogen source for HDO. Water splitting over metallic surfaces is attracting great interests

within the catalytic community and it would be worth exploring its coupling with HDO. Nevertheless, the regeneration of the active metal generally needs fairly high temperatures, what is a strong drawback of this route. The deactivation of the catalyst under the reaction media during water splitting coupled to hydrodeoxygenation also rises concerns for this strategy. In this sense, progress in catalysis science and biomass processing technologies seems to share a common destiny which brings hopes to a greener future using renewable sources for clean energy and chemicals production.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Hydrodeoxygenation · biomass model compounds · HDO catalyst · reforming · catalytic transfer hydrogenation · metal hydrolysis · non-thermal plasma

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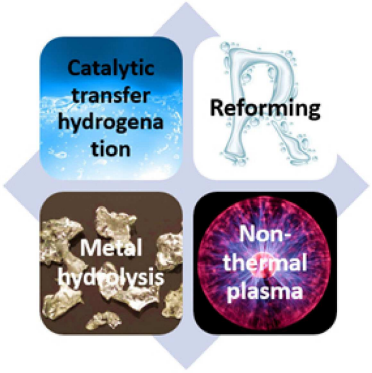
REVIEWS

The development of hydrogen-free alternatives to facilitate oxygen removal in biomass derived compounds is a major challenge for catalysis science but at the same time it could revolutionize biomass processing technologies. In this review, several novel approaches are analysed. The current challenges and research trends of novel hydrodeoxygenation strategies are also presented aiming to spark inspiration among the broad community of scientists working towards a low carbon society where bio-resources will play a major role.



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